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DETERMINATION OF AOX REMOVAL EFFICIENCY IN THE WASTEWATER
TREATMENT SYSTEM AT THE ALBERTA-PACIFIC FOREST INDUSTRIES
KRAFT PULP MILL

by

Shaun Bruce McNameara



A thesis submitted to the Faculty of Graduate Studies and Research in partial
fulfillment of the requirements for the degree of Master of Science

in

Environmental Science

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University of Alberta

Faculty of Graduate Studies and Research

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled **Determination of AOX Removal Efficiency in the Wastewater Treatment System at the Alberta-Pacific Forest Industries Kraft Pulp Mill** submitted by **Shaun Bruce McNamara** in partial fulfillment of the requirements for the degree of **Masters of Science in Environmental Science**.



For the girls who helped make this possible:
Kerry, Caelan, Baba, Mom, Lorna, Jeanie

ABSTRACT

A high performing wastewater treatment system at a bleached kraft pulp mill was evaluated to understand the efficiency of adsorbable organic halogen (AOX) removal. A hydraulic retention study was initially undertaken so that wastewater testing could follow the flow of wastewater through the system and evaluate removal across each unit process. AOX removal efficiency was compared to removal efficiency of other wastewater parameters, to operating conditions, and to other wastewater characteristics. It was found that AOX removal was occurring in all stages of the wastewater treatment system. In particular, removal in the primary clarifiers was very high (43%) and the activated sludge treatment process was performing at a very high level (70% removal). Neutralization using caustic, the return of waste activated sludge (WAS) to the front of the system, and the high sludge age are believed to be major factors in the systems performance.

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TABLE OF CONTENTS

1. INTRODUCTION	1
1.1 BACKGROUND	1
1.2 ALBERTA-PACIFIC PULP MILL OVERVIEW	4
1.2.1 <i>Pulping Process</i>	4
1.2.2 <i>Wastewater Treatment</i>	8
1.2.2.1 Process Description	8
1.2.2.2 Theoretical Hydraulic Retention Times	11
2. LITERATURE REVIEW	12
2.1 AOX: DISCUSSION	12
2.1.1 <i>AOX Sources and Characteristics</i>	12
2.1.2 <i>AOX Methodology</i>	13
2.2 LEGISLATION	17
2.2.1 <i>Alberta Legislation</i>	17
2.2.2 <i>Canadian Legislation</i>	19
2.2.3 <i>International Legislation</i>	19
2.2.4 <i>Using Wastewater Treatment to Meet Discharge Limits</i>	20
2.3 AOX REMOVAL IN VARIOUS WASTEWATER TREATMENT SYSTEMS	21
2.3.1 <i>Primary Treatment</i>	21
2.3.2 <i>Secondary Treatment</i>	22
2.4 COMPARISON OF AOX DISCHARGES BETWEEN ALBERTA KRAFT PULP MILLS	22
3. OBJECTIVES.....	24
4. MATERIALS AND METHODS.....	25
4.1 SAMPLE LOCATIONS	25
4.2 TIMING OF SAMPLE COLLECTION	26
4.2.1 <i>Retention Study Methodology</i>	26
4.3 OPERATING REQUIREMENTS.....	27
4.3.1 <i>Wastewater Treatment System Operations</i>	27
4.3.2 <i>Pulp Mill Operations</i>	27
4.4 TESTING PERFORMED	28
4.5 ANALYSIS METHODS	29
4.5.1 <i>Sample Collection and Storage</i>	29
4.5.2 <i>AOX Methodology</i>	29
4.5.3 <i>COD Methodology</i>	30
4.5.4 <i>Organic Carbon Methodology</i>	30
4.5.5 <i>Total Suspended Solids Methodology</i>	30
4.5.6 <i>BOD₅ Methodology</i>	30
4.5.7 <i>Colour Methodology</i>	31
5. RESULTS.....	32

5.1 OVERVIEW.....	32
5.2 RETENTION STUDY	32
5.2.1 <i>Primary Clarifier Retention Time</i>	32
5.2.2 <i>Equalization/Cooling Pond Retention Time</i>	33
5.2.3 <i>Bioreactor Retention Time</i>	34
5.2.4 <i>Secondary Clarifier Retention Time</i>	36
5.3 SLUG RESULTS	38
5.3.1 <i>Distribution Box #1 Results</i>	38
5.3.2 <i>Distribution Box #3 Results</i>	39
5.3.3 <i>Cooling Tower Results</i>	40
5.3.4 <i>Distribution Box #5 Results</i>	41
5.3.5 <i>Parshall Flume Results</i>	42
5.3.6 <i>Results-Overview of Edited Data</i>	43
6. DISCUSSION.....	44
6.1 RETENTION STUDY RESULTS	44
6.1.1 <i>Primary Clarifier Hydraulic Retention Time</i>	44
6.1.2 <i>Equalization/Cooling Pond Hydraulic Retention Time</i>	45
6.1.3 <i>Bioreactor Hydraulic Retention Time</i>	47
6.1.4 <i>Secondary Clarifier Hydraulic Retention Time</i>	48
6.2 LOCATION OF AOX REMOVAL	48
6.2.1 <i>Removal Summary</i>	48
6.2.2 <i>Primary Clarification Removal</i>	50
6.2.3 <i>Equalization/Cooling Pond Removal</i>	53
6.2.4 <i>Bioreactor and Secondary Clarification Removal</i>	54
6.2.5 <i>Total System Performance</i>	58
7. CONCLUSIONS.....	61
8. RECOMMENDATIONS	62
9. REFERENCES	63
10. APPENDIX A: MONITORING REQUIREMENTS FOR AL-PAC WASTEWATER.....	67
11. APPENDIX B: SUMMARY OF RESULTS—UNEDITED DATA.....	69
12. APPENDIX C: SUMMARY OF RESULTS—EDITED DATA	75
13. APPENDIX D: SAMPLING TIMES.....	81
14. APPENDIX E: HYDRAULIC RETENTION TIMES.....	83

15.	APPENDIX F: RETENTION STUDY DATA.....	85
16.	APPENDIX G: PICTURES OF SAMPLING LOCATIONS.....	91
17.	APPENDIX H: AERIAL VIEW OF MILLSITE	95

List of Tables

Table 1.1: Theoretical wastewater treatment system hydraulic retention times.....	11
Table 2.1: Structural features of high molecular mass chlorolignin material. (Fleming <i>et al.</i> 1990).....	13
Table 2.2: Summary of AOX methods.....	16
Table 2.3: Sample preservation	17
Table 2.4: Discharge standards for Alberta pulp mills (Alberta Environment, 2002)	18
Table 2.5: AOX limit comparison	19
Table 2.6: Alberta kraft pulp mill AOX discharge comparison for 2001.	23
Table 4.1: Sampling locations	25
Table 5.1: Wastewater treatment system hydraulic retention times.....	32
Table 5.2: Results of slug 6 BOD ₅ results for cooling tower sample.....	40
Table 5.3: Results of slug 11 and slug 12 BOD ₅ for the cooling tower sample.....	41
Table 6.1: Expected wastewater treatment system hydraulic retention times based on retention study	44
Table 6.2: AOX result summary	49
Table 6.3: AOX removal summary	49
Table 6.4: Summary of system performance.....	59
Table 6.5: Colour removal.....	60
Table 10.1: Al-Pac monitoring requirements for industrial wastewater	68
Table 11.1: Results of testing at distribution box #1 (unedited)	70
Table 11.2: Results of testing at distribution box #3 (unedited)	71
Table 11.3: Results of testing at the cooling tower (unedited).....	72
Table 11.4: Results of testing at distribution box #5 (unedited)	73
Table 11.5: Results of testing at the parshall flume (unedited).....	74
Table 12.1: Results of testing at distribution box #1 (edited)	76
Table 12.2: Results of testing at distribution box #3 (edited)	77
Table 12.3: Results of testing at the cooling tower (edited).....	78
Table 12.4: Results of testing at distribution box #5 (edited)	79
Table 12.5: Results of testing at the parshall flume (edited).....	80
Table 13.1: Sample times	82
Table 14.1: Hydraulic retention time summary for each sample slug.....	84
Table 15.1: Primary clarifier retention fluorescence data	86
Table 15.2: Equalization/cooling pond retention fluorescence data	87
Table 15.3: Bioreactor retention fluorescence data	88
Table 15.4: Secondary clarifier retention fluorescence data	90

List of Figures

Figure 1.1: 1999 AOX discharges for bleached kraft mills (adapted from EKONO/Duoplan Multi-Client Study 2001).....	2
Figure 1.2: Fibreline process diagram—digester and brownstock areas at Alberta-Pacific Forest Industries	6
Figure 1.3: Fibreline process diagram—bleach plant at Alberta-Pacific Forest Industries	7
Figure 1.4: Wastewater treatment system at Alberta-Pacific Forest Industries	10
Figure 2.1: The AOX method (Odendahl <i>et al.</i> 1990)	15
Figure 5.1: Primary clarifier retention response curve	33
Figure 5.2: Equalization/cooling pond retention response curve	34
Figure 5.3: Wastewater flow during bioreactor retention study.....	35
Figure 5.4: Bioreactor retention response curve.....	36
Figure 5.5: Secondary clarifier retention response curve.	37
Figure 5.6: Wastewater flow during secondary clarifier retention study.	37
Figure 6.1: Theoretical HRT for a CFSTR and plug flow reactor the same volume as the equalization/cooling pond.....	46
Figure 6.2: Theoretical HRT for a CFSTR and plug flow reactor the same volume as the bioreactors	47
Figure 6.3: Relationship between influent TSS and soluble AOX removal.....	52
Figure 6.4: Relationship between HRT in primary clarifiers and soluble AOX removal	52
Figure 6.5: Effect of secondary treatment influent concentration on removal efficiency.	56
Figure 6.6: Secondary treatment total AOX removal efficiencies versus other organic removal efficiencies.....	57
Figure 6.7: Secondary treatment colour removal relation with soluble AOX removal.....	58
Figure 16.1: Sampling at distribution box #1	92
Figure 16.2: Sampling at distribution box #3	92
Figure 16.3: Sampling at cooling tower	93
Figure 16.4: Sampling at distribution box #5	93
Figure 16.5: Sampling at parshall flume.	94
Figure 17.1: Aerial picture of the Alberta-Pacific pulp mill including the wastewater treatment system.	96

List of Abbreviations

μg	Microgram
μm	Micrometer (micron)
ADt	Air Dried Tonne
Al-Pac	Alberta Pacific Forest Industries
AOX	Adsorbable Organic Halogens
BKP	Bleached Kraft Pulp
BOD	Biochemical Oxygen Demand
BOD ₅	5-day Biochemical Oxygen Demand
Cl ₂	Chlorine
ClO ₂	Chlorine Dioxide
CO ₂	Carbon Dioxide
CFSTR	Continuous Flow Stirred-Tank Reactor
CT	Cooling Tower
CTMP	Chemithermomechanical Pulp
CU	Colour Unit
DB#1	Distribution Box #1
DB#3	Distribution Box #3
DB#5	Distribution Box #5
DIN	German Industrial Standard
DO	Dissolved Oxygen
DOC	Dissolved Organic Carbon
ECF	Elementally Chlorine Free
EMCC	Extended Modified Continuous Cook
E _{OP}	Alkaline Extraction using oxygen and hydrogen peroxide
GAG	Granular Activated Carbon
H ₂ O	Water
H ₂ SO ₄	Sulphuric Acid
HCl	Hydrochloric Acid
HRT	Hydraulic Retention Time
L	Litre
m ³	Cubic meter
mg	Milligram
mL	Millilitre
MLSS	Mixed Liquor Suspended Solids
Na ₂ S	Sodium Sulphide
Na ₂ SO ₃	Sodium Sulphite
NaOH	Sodium Hydroxide
NCASI	National Council for Air and Stream Improvement, Inc.
O ₂	Oxygen
PAPRICAN	Pulp and Paper Research Institute of Canada
PAPTAC	Pulp and Paper Technical Association of Canada
ppb	Parts Per Billion
RAS	Return Activated Sludge

SOC	Suspended Organic Carbon
TCF	Total Chlorine Free
TMP	Thermomechanical Pulp
TOC	Total Organic Carbon
TSS	Total Suspended Solids
USEPA	United States Environmental Protection Agency
WAS	Waste Activated Sludge

1. INTRODUCTION

1.1 Background

In 1988, Crestbrook Forest Industries Ltd. proposed to the government of Alberta “the most up-to-date and appropriate combination of process techniques then available” for the Alberta-Pacific Forest Industries bleached kraft pulp mill (Alberta-Pacific Forest Industries Inc. 1990). However, in the March 1990 report from the Alberta-Pacific Environmental Impact Assessment Review Board, the board recommended that the proposed mill not be approved, primarily due to the content of chlorinated organic compounds in the wastewater, and the cumulative effects on the Athabasca-Peace River system (Alberta-Pacific Environmental Impact Assessment Review Board. 1990).

In order to address these concerns, the mill was redesigned so as not to use elemental chlorine in its bleaching process. With these process changes and an activated sludge wastewater treatment system, expected chlorinated organics in the final wastewater would be reduced to acceptable standards.

One effective means of estimating the level of chlorinated organics in the wastewater is by using the AOX (adsorbable organic halogen) test. The proposed mill design predicted AOX levels in the final wastewater discharge of less than 0.25 kg/ADt (Alberta-Pacific Forest Industries Inc. 1990), based on expected removal efficiencies in wastewater treatment of about 45% for both hardwood and softwood (Alberta-Pacific Scientific Review Panel 1990). Alberta-Pacific’s wastewater treatment system, however, is seeing removal efficiencies that are much higher. This performance is approximately twice of the expected 45% and has resulted in Alberta Pacific’s AOX discharges being among the lowest in the world. Figure 1.1 compares the 1999 discharge from Canadian pulp mills to the discharge from other mills in the United States, Sweden, and Finland.

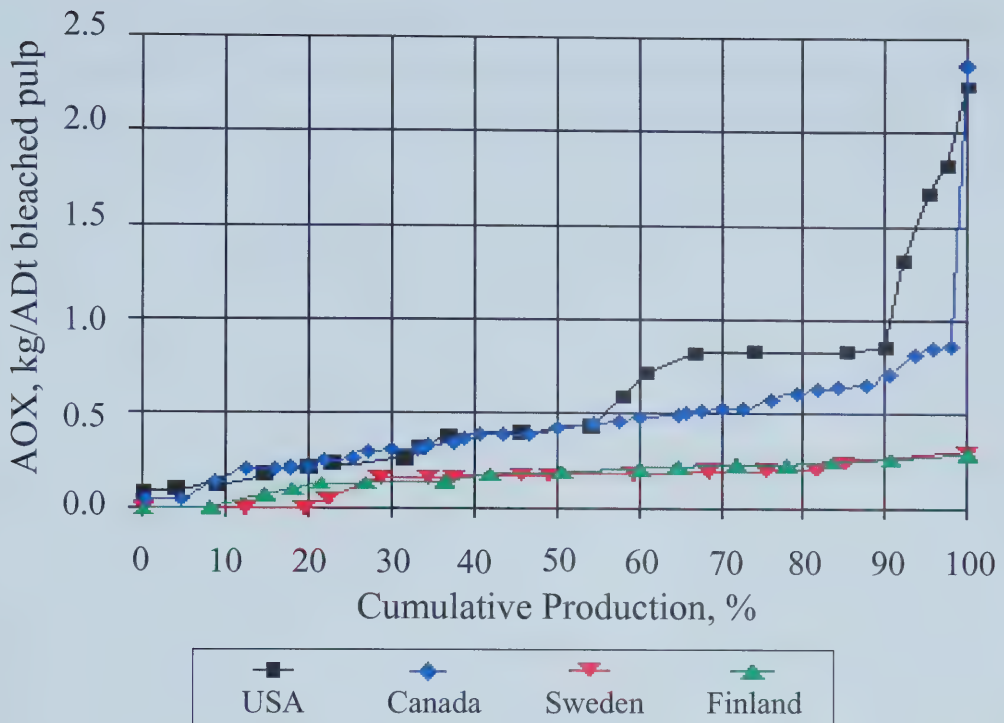


Figure 1.1: 1999 AOX discharges for bleached kraft mills (adapted from EKONO/Duoplan Multi-Client Study 2001)

In Figure 1.1 each marker on the chart represents a bleached kraft pulp mill. In Canada, AOX discharges range from very low (just above zero) to about 4.5 kg/ADt. Excluding the worst Canadian mill, the upper range is below 1.0 kg/ADt. The AOX discharges of Canadian mills are distributed evenly within this range. The Swedish and Finnish mills are all very similar with regards to AOX discharges, with no bad performers (all below 1.0 kg/ADt). The mills in the United States of America can be broken into three main groups according to the above chart. About 55% of the production is in mills with AOX discharges of less than 0.5 kg/ADt, about 35% of the production is in mills with AOX discharges of between 0.5 kg/ADt and 1.0 kg/ADt, and about 10% of the production is in mills with AOX discharges greater than 1.0 kg/ADt.

The extraordinary performance of the wastewater treatment system at Alberta-Pacific is little understood. This research was undertaken to provide more information of AOX removal specifically in Alberta-Pacific's wastewater treatment system.

1.2 Alberta-Pacific Pulp Mill Overview

1.2.1 Pulping Process

The Alberta-Pacific Forest Industries pulp mill began operations in September of 1993. It is a kraft (sulphate) mill, which means it uses a chemical solution consisting primarily of sodium sulphide (Na_2S) and sodium hydroxide (NaOH) called *white liquor* to dissolve lignin from wood. The mill pulps hardwood (primarily aspen) about 90% of the time and softwood (primarily spruce) about 10% of the time. Design for hardwood production is 1500 air dried tonnes (ADt) per day and design for softwood production is 1250 ADt per day.

The technology used is among the environmentally friendliest in the world. The use of a Kamyr EMCC (extended modified continuous cook) digester and oxygen delignification enable a very low kappa number to enter the bleach plant (about 7 to 9 for hardwood). The kappa number is a standard measurement in the kraft pulp industry of the amount of lignin remaining in a pulp sample. This low kappa number enables the bleach plant to be elementally chlorine free (ECF). The use of chlorine dioxide (ClO_2) instead of molecular chlorine reduces the formation of harmful chlorinated organic compounds, and virtually eliminates the formation of chlorinated dioxins and chlorinated furans. A bleaching sequence of $\text{DE}_{\text{OP}}\text{D}$ is currently used, though the mill has the ability to run as $\text{DE}_{\text{OP}}\text{DD}$. The bleaching sequence refers to each stage of bleach plant. D refers to use of 100% chlorine dioxide. E_{OP} refers to caustic extraction (E) using oxygen (o) and hydrogen peroxide (p). Other common notations used include C (elemental chlorine), H (hypochlorite) and Z (ozone). Each capital letter refers to a bleach stage which is followed by a wash. If the letters are enclosed by parentheses, then this indicates that there is only one wash for these stages in total. For example, $\text{DE}_{\text{OP}}(\text{DED})$ is a three wash process. Figure 1.2 and Figure 1.3 show the fibreline process flow.

Bleached pulp from the fibreline is sent to the machine room for finishing. Here the pulp is formed into a sheet and 90% of the water is removed (90% dried is equivalent

to 100% air dried). It is then cut up and stacked into bales. The finished bales are sent around the world to be used in photographic paper, writing paper, Bible paper, cigarette paper, and tissue paper, among others.

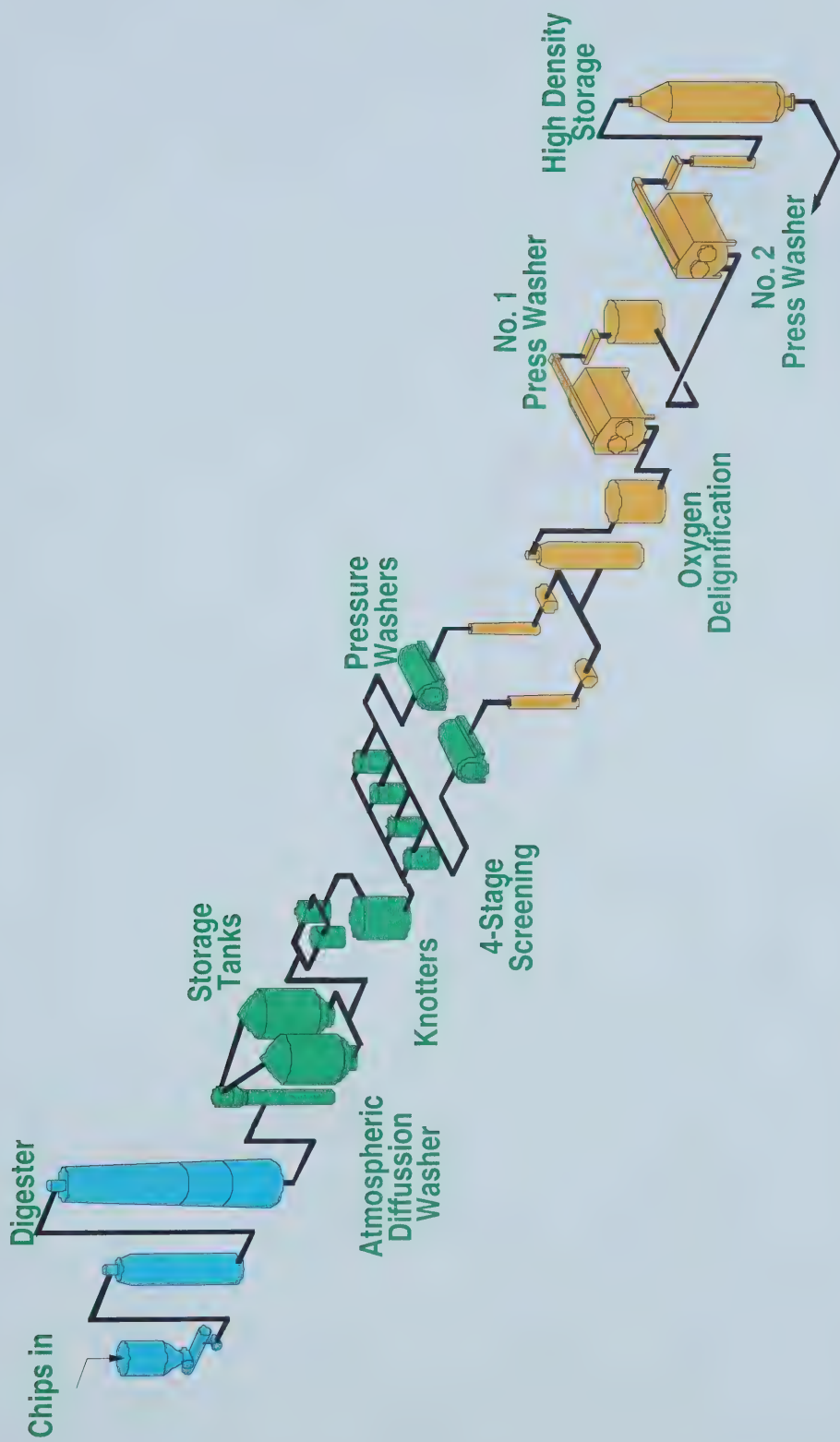


Figure 1.2: Fibreline process diagram—digester and brownstock areas at Alberta-Pacific Forest Industries

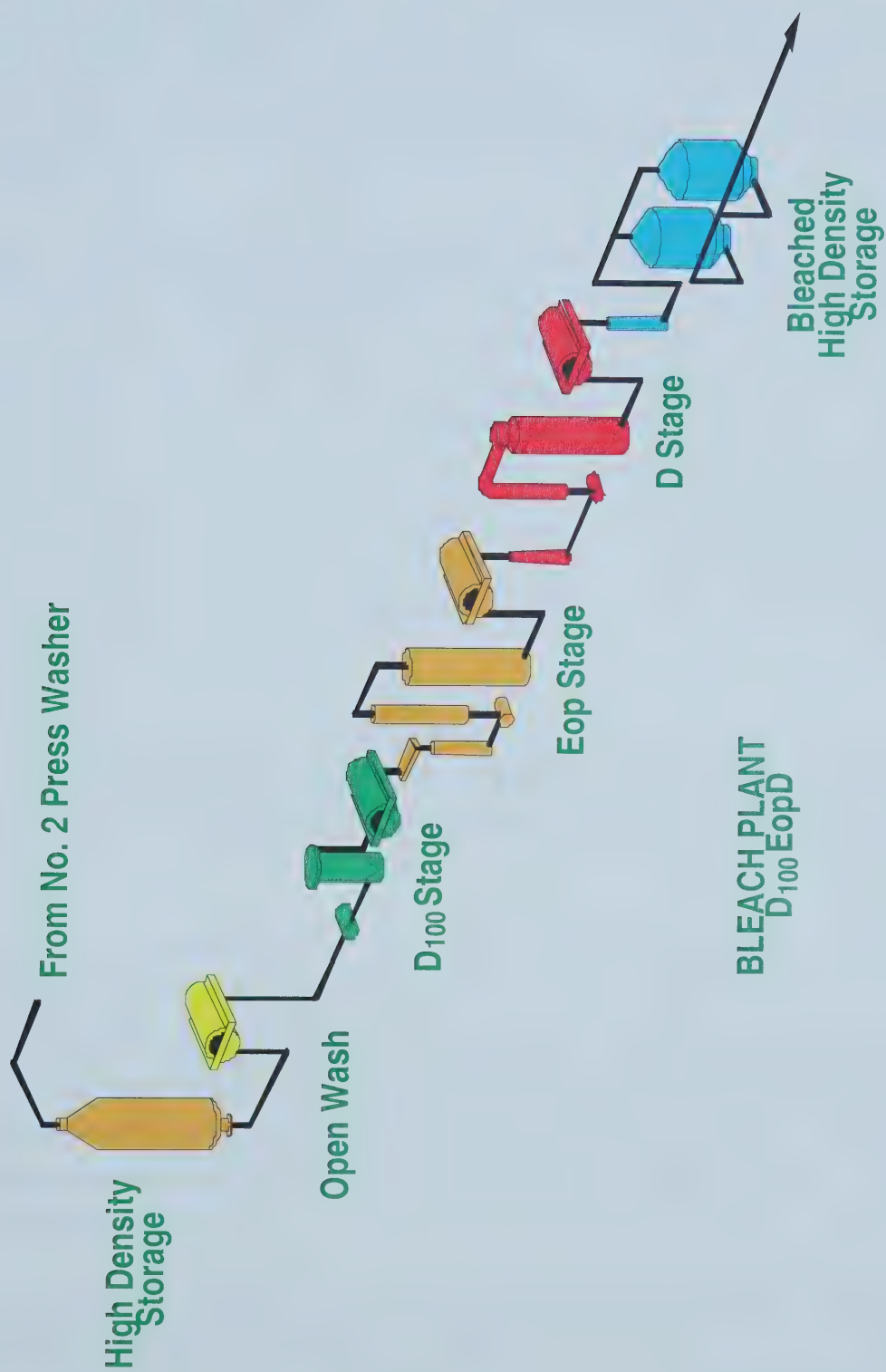


Figure 1.3: Fibreline process diagram—bleach plant at Alberta-Pacific Forest Industries

1.2.2 Wastewater Treatment

1.2.2.1 Process Description

The wastewater is treated in three basic stages: preliminary, primary, and secondary treatment.

Preliminary treatment consists of neutralization and screening. Neutralization is first done by combining the acid and alkaline wastewaters from the mill, then by adding 97% sulphuric acid (H_2SO_4) or 10% caustic soda (NaOH) if necessary to achieve the desired pH. There is also a provision for adding lime dust slurry from the lime kiln precipitator catch slurry tank to the bleach plant acid sewer. Some other mill wastewater streams, such as waste activated sludge, storm pond collection (site runoff), and backwash from the water treatment filters, are combined with the neutralized mill wastewater following the neutralization chamber. The wastewater stream is then screened to remove large solids. The solids are collected in the solids holding bin to be disposed of in the landfill.

A spill pond located downstream of the screening building allows for temporary diversion of mill spills or excess flows. Normally a poorer quality wastewater, it can be slowly brought back into the wastewater treatment system to avoid shocking the system.

Primary treatment consists of solids removal using clarifiers that provides retention time to provide a laminar settling zone for settling by gravity. The clarified wastewater is then sent to the equalization/cooling pond, and the solids (sludge) are sent to the sludge handling process. The equalization/cooling pond provides mixing and aeration that both cools the wastewater and ensures a more homogenous stream enters secondary treatment. This equalization/cooling pond does not provide hydraulic equalization.

A cooling tower can provide extra cooling if necessary, or may be bypassed. This is normally only used during the summer months.

From the cooling tower the wastewater is mixed with return activated sludge (RAS) from the secondary clarifiers, and then split into two bioreactors. The activated sludge (aerobic bacteria) in the bioreactors degrades the contaminants in the wastewater using oxygen provided through aeration. Each bioreactor is divided into 5 cells, which are fed in ascending order, although flexibility in the design allows for wastewater feed to cell 1 or cell 3 or any combination of cell 1 or cell 3. The design of the activated sludge process at Al-Pac is commonly referred to as extended aeration activated sludge. This design allows for a long hydraulic retention time (HRT) and results in lower sludge production.

Wastewater from the two bioreactors will mix and then enter the secondary clarifiers to remove the solids (activated sludge). This process is similar to the primary clarification process except that the characteristics of the solids are quite different. The sludge from the secondary clarifiers consists primarily of the bacteria that consume the organics in the wastewater of the bioreactors. This sludge is either returned to the front of the bioreactors (return activated sludge, RAS) or wasted to the front of the primary clarifiers (waste activated sludge, WAS). Typical recycle rates at Al-Pac are in the range of 0.30 to 0.40 m³/s, and typical wasting rates are in the range of 0.005 to 0.007 m³/s. The concentration of these sludge streams is normally 9 to 17 kg/m³. The practice of wasting sludge into the primary clarifiers is not common practice in most other activated sludge systems.

The clarified wastewater flows to the head pond, which acts to prevent air from entering the pipe carrying the wastewater to the river by use of an automated valve which ensures the pipe is always full.. Air in the pipe can cause foaming upon diffusion to the river. A 5.5 kilometre pipe carries the wastewater to the river where it is discharged through submerged diffusers. Figure 1.4 shows an overview of the wastewater treatment system.

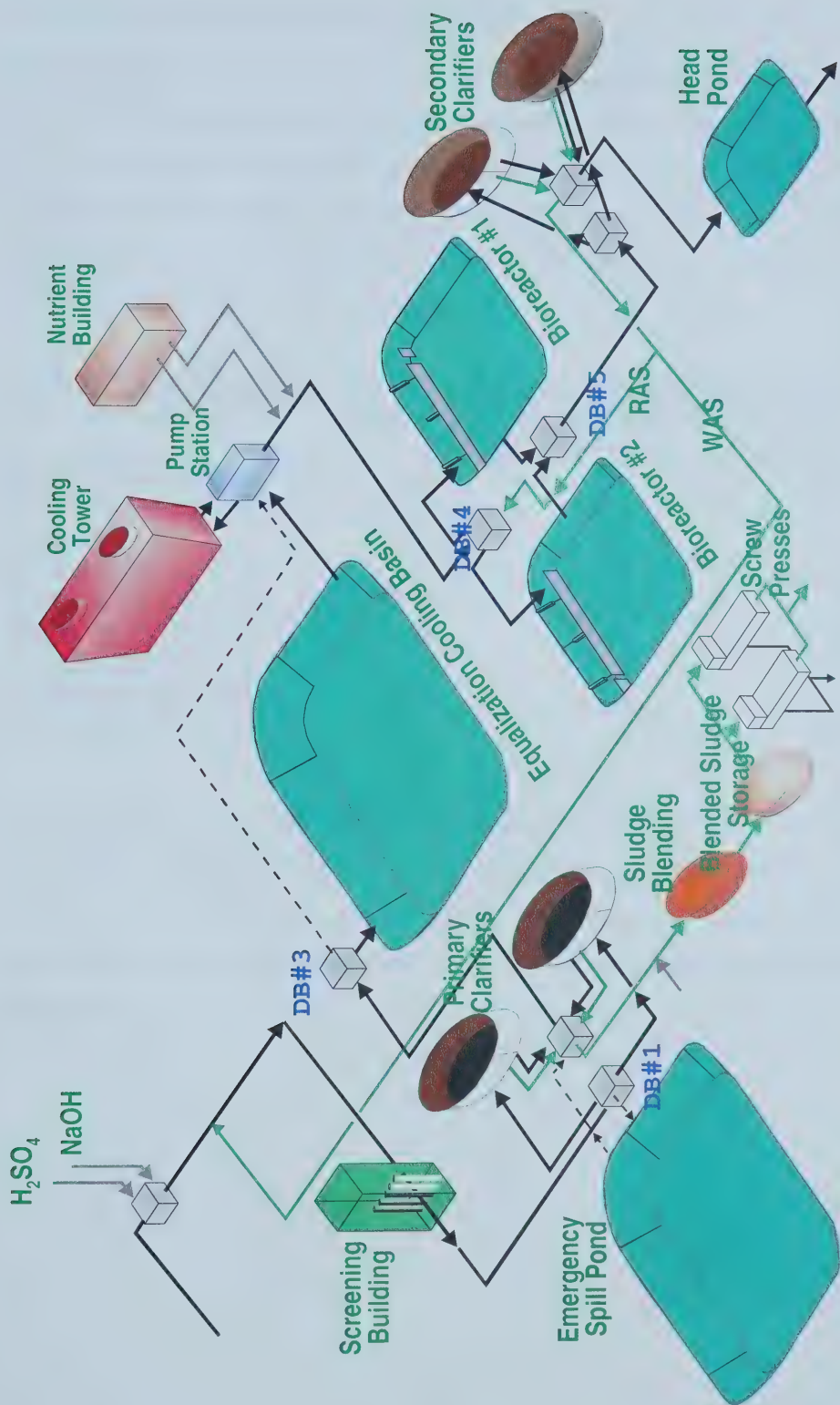


Figure 1.4: Wastewater treatment system at Alberta-Pacific Forest Industries

1.2.2.2 Theoretical Hydraulic Retention Times

Theoretical hydraulic retention times are based on a design flow of $0.80 \text{ m}^3/\text{s}$ ($69,120 \text{ m}^3/\text{day}$) of wastewater and $0.60 \text{ m}^3/\text{s}$ of return activated sludge, and are listed in Table 1. The theoretical retention times for the equalization/cooling pond and the bioreactor cells are taken from Process and Control diagrams for the wastewater treatment plant, as provided by the mill designer, H.A. Simons Ltd.. The retention times for the clarifiers are based on a plug flow design.

Table 1.1: Theoretical wastewater treatment system hydraulic retention times

Process Unit	Volume (m^3)	Design Influent Flow (m^3/s)	Design Retention Time (hours)
Primary Clarification	19,440	0.8	6.8
Equalization/Cooling Pond	86,400	0.8	24.0
Bioreactor Cell 1	7,600	1.4	2.6
Bioreactor Cell 2	5,600	1.4	1.8
Bioreactor Cell 3	5,600	1.4	1.8
Bioreactor Cell 4	6,400	1.4	2.2
Bioreactor Cell 5	84,400	1.4	29.3
Secondary Clarification	25,600	1.4	5.1
Total			73.6

The typical flows are slightly higher (approximately $72,000 \text{ m}^3/\text{day}$ or $0.83 \text{ m}^3/\text{s}$) than the design of the facility. The influent flow to the bioreactors and secondary clarifiers also includes the RAS flow, which is typically about $0.35 \text{ m}^3/\text{s}$. Volumes not mentioned, such as pipes, the cooling tower, and distribution boxes are considered insignificant.

2. LITERATURE REVIEW

The bulk of literature on AOX (adsorbable organic halogen) was published in the late 1980's and early 1990's when there was a heightened awareness of the environmental impacts from elemental chlorine bleaching. There has been recent interest, though, as the provincial governments of Quebec, Ontario, and British Columbia have made changes to the regulations regarding this parameter. Although the interest in this parameter has lessened, it will continue to be a key measure of a pulp mill environmental impact for years to come.

2.1 AOX: Discussion

The AOX parameter is a measure of the total quantity of organically bound halogens that are adsorbed onto a bed of activated carbon over which a wastewater sample is passed. In this case, AOX is essentially a measure of organochlorine in bleached kraft mill wastewaters, since the content of other halogens is negligible (McKinnon 1992). It is a concern because of the perceived links between chlorinated organic compounds and toxicity.

2.1.1 AOX Sources and Characteristics

In pulp mills, chlorinated organic compounds are formed during the bleaching process when chlorine and/or chlorine dioxide are added to the pulp. They are produced primarily as a result of complex reactions occurring between the chlorine bleaching agent and the residual lignin (5 to 10%) remaining in the pulp (Fleming *et al.* 1990). Molecular chlorine depolymerizes lignin by oxidizing the aromatic rings of its residues to produce an array of soluble, structurally diverse compounds (McKinnon 1992). Chlorine dioxide bleaching sequences can also form chlorinated organic compounds since some elemental chlorine is present in each stage, either as a by-product of chlorine dioxide generation, or as a product of reaction.

In pulp mill wastewater, AOX consists of approximately 80% high molecular mass materials (> 1000 dalton), leaving approximately 20% low molecular mass compounds (< 1000 dalton) (McCubbin and Folke 1993). The high molecular mass compounds (chlorolignin) are difficult to analyze using commonly employed analytical tools such as gas chromatography and mass spectrometry. However, the *general* structure of chlorolignins have been determined using other analysis techniques (Fleming *et al.* 1990). These features are summarized in Table 2.1.

Table 2.1: Structural features of high molecular mass chlorolignin material. (Fleming *et al.* 1990)

-
- High carbonyl and carboxyl content and low methoxyl and phenolic hydroxyl contents relative to that found in unchlorinated lignin.
 - Carbonyl groups conjugated with double bonds are common
 - Mainly non-aromatic lignin oxidation products
 - Percentage of organically bound chlorine is 8 to 16%
-

McKague *et al.* (1998) have identified 329 chlorinated compounds in chlorine based bleaching, 87 chlorinated compounds from elemental chlorine free (ECF) bleaching, and one chlorinated compound from totally chlorine free (TCF) bleaching.

Although only comprising about 20% of the total AOX, it is the low molecular weight portion that is of environmental significance because of their ability to penetrate biological membranes (McKinnon 1992). There have been over 300 low molecular weight compounds identified in bleach plant filtrates (NCASI 1990).

2.1.2 AOX Methodology

The AOX procedure involves five basic steps:

- 1) dilution,
- 2) adsorption,
- 3) rinse,
- 4) combustion, and
- 5) microcoulometric determination.

Because the working range of the instrumentation is 25 to 400 µg/L, almost all kraft mill wastewater samples must be diluted to within this range. This usually involves a series of dilutions using dilute nitric acid.

Adsorption is done using either the shaker method or with the column method.

Granular activated carbon (GAC) is used as the adsorbent. In the shaker method, an appropriate volume of sample is added to about 40 mg of GAC in a 250 mL Erlenmeyer flask. The flask is then shook on a shaking apparatus for ½ to 1 hour. The contents of the flask are then filtered through a 0.40 µm polycarbonate membrane filter to separate the GAC from the wastewater. The GAC is then rinsed with a nitrate solution to remove any inorganic halogens. In the column method, the sample is passed through a column of GAC. The column is then rinsed with a nitrate solution as above.

The GAC (and the filter, if used) are then combusted in a pyrolysis oven at 950°C (under an atmosphere of oxygen). Product gases are bubbled through an electrolyte and hydrogen chloride (HCl) is dissolved. A microcoulometric titration determines the chloride (actually halogen) concentration.

Odendhal *et al.* view the analysis as a three-step process. Figure 2.1 outlines the AOX methodology.

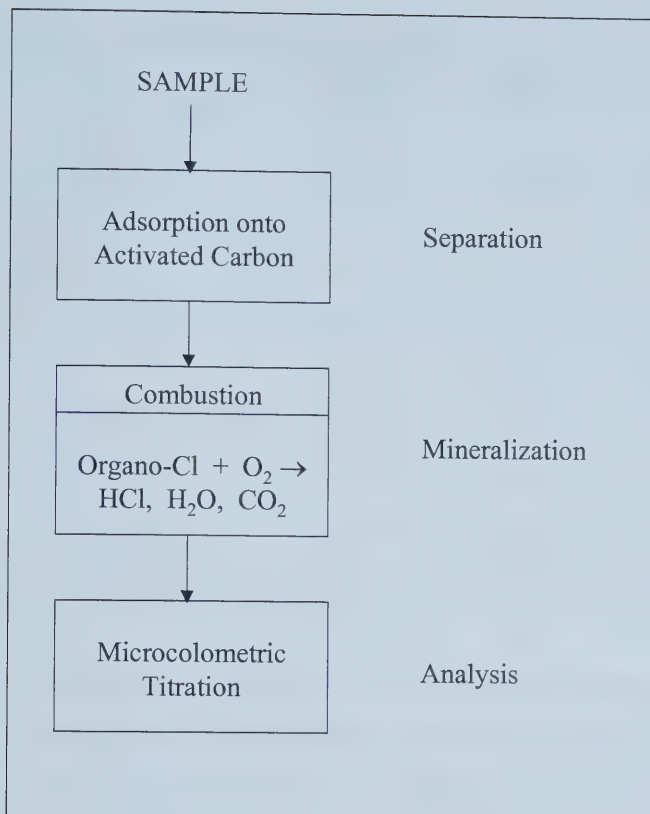


Figure 2.1: The AOX method (Odendahl *et al.* 1990)

There are many different AOX methods being used in the world today. All of them use the methodology described above. Table 2.2 lists some of the methods.

Table 2.2: Summary of AOX methods

Source	Number	Name	Date
Standard Methods United States	5320	Dissolved Organic Halogen	1998
Environmental Protection Agency	9020B	Total Organic Halides (TOX)	1994
Alberta Environmental Protection	AE 128.1	Adsorbable Organic Halides in Pulp Mill Wastewater	1992
German Standard	DIN 38409	Determination of Extractable Organically Bonded Halogens (EOX) Reference Method for the	1985
Environment Canada and PAPRICAN	EPS 1/RM/16	Determination of Adsorbable Organic Halogens (AOX) in Waters and Wastewaters	1992
Scandinavian Pulp, Paper, and Board Testing Committee	SCAN-W 9:89	Organically Bound Chlorine by the AOX Method	1989

These methods can differ, however. The most significant differences include the way the sample is preserved between sampling and analysis. Whereas all the methods in Table 2.2 require that the sample bottles are filled with no headspace and storage at 4°C, other preservation differences exist. Most methods require protection from light by use of an amber bottle or storage in the dark. Method AE 128.1 and Method DIN 38409 do not make mention of this. The addition of sodium sulphite (Na_2SO_3) to react with chlorine is also recommended, although some only suggest adding Na_2SO_3 only if residual chlorine exists. Slight differences exist between the methods in relation to the acidification of the sample and the maximum recommended storage time. These differences are summarized in Table 2.3.

Table 2.3: Sample preservation

Method	Acidification	Storage Time
5320	pH 2 using nitric acid	< 14 days
9020B	pH < 2 using sulphuric acid	< 28 days
AE 128.1	pH 1.5 to 2.1 using nitric acid	< 21 days
DIN 38409	pH 2 to 3 using nitric acid	Examine as rapidly as possible.
EPS 1/RM/16	pH 1.5 to 2.0 using nitric acid	Only requires that the storage time be reported
SCAN-W 98:9	pH 1.5 to 2.1 using nitric acid	Should be analysed on day of sample or frozen.

2.2 Legislation

2.2.1 Alberta Legislation

Alberta-Pacific Forest Industries' current AOX limitation is a maximum daily of 1390 kg of AOX per day based on a 24-hour composite sample. The maximum daily average for any month cannot exceed 818 kg (Alberta Environmental Protection 1996). The maximum daily limit works out to about 0.55 kg/ADt (based on 1500 ADt/day) or 0.49 kg/ADt (based on 2002 actual production of 1662 ADt/day).

The Government of Alberta does not have a general AOX limitation that covers all of the kraft pulp mills in the province (there are four), but rather limitations based on each mill. The AOX limits, as well as other discharge standards, of all the other Alberta pulp mills are summarized on Table 2.4.

Alberta Environment's concept of "due diligence" works to reduce AOX emissions because mills are legally required to operate as efficiently as possible. Section 215 of the Alberta Environmental Protection and Enhancement Act (Province of Alberta 1996) says "No person shall be convicted of an offence...if that person establishes on a balance of probabilities that he took all reasonable steps to prevent its commission". This defence is a major incentive for preventative and preparative actions.

Table 2.4: Discharge standards for Alberta pulp mills (Alberta Environment, 2002)

Pulp Mill	Pulp Type	Compliance Schedule	BOD		TSS		AOX		Colour	
			kg/day	kg/ADt	kg/day	kg/ADt	kg/day	kg/ADt	kg/day	kg/ADt
Alberta Newsprint Company (Whitecourt)	TMP Newsprint	1998	2100	3.0	3500	5.0	NA	NA	31500	45
Alberta-Pacific Forest Industries (Athabasca)	BKP	1996	2250	1.5	4500	3.0	818	0.55	104000	69
Daishowa-Marubeni (Peace River)	BKP	May 1, 1998 Jan. 1, 2000	4050 4050	3.0 3.0	6750 6750	5.0 5.0	1400 880	1.04 0.65	182000 121500	135 90
Millar Western (Whitecourt)	CTMP	1994	2040	3.0	3400	5.0	NA	NA	30600	45
Slave Lake Pulp (Slave Lake)	CTMP	1994	1050	2.6	2000	5.0	NA	NA	18000	45
Weldwood (Hinton)	BKP	1998	3300	3.0	5500	5.0	800	0.73	60000	55
Weyerhaeuser (Grande Prairie)	BKP	Jul. 1, 1997	2460	3.0	4100	5.0	1230	1.50	73800	90
		Jul. 1, 2002	2460	3.0	4100	5.0	1230	1.50	50000	61
		Mar. 1, 2007	2460	3.0	4100	5.0	1230	1.50	37400	46

Notes: ADt = Air Dried Tonnes of Pulp

BKP = Bleach Kraft Pulp

CMTP = Chemithermomechanical Pulp

TMP = Thermomechanical Pulp

BOD = Biochemical Oxygen Demand

TSS = Total Suspended Solids

AOX = Adsorbable Organic Halides

Colour: 1 CU = 1 mg/L for the determination of
kg/day and kg/ADt

kg/ADt is based on reference production capacity only, not actual production

Actual monthly and daily limits are in kg/day

2.2.2 Canadian Legislation

There are no federal limitations on AOX, but other regulations that are in place work indirectly to reduce the discharge of AOX compounds. The Pulp and Paper Mill Wastewater Chlorinated Dioxins and Furans Regulations (Department of the Environment 1992) requires that no measurable levels of 2,3,7,8-tetrachlorodibenzo-para-dioxin (2,3,7,8-TCDD) or 2,3,7,8-tetrachlorodibenzofuran (2,3,7,8-TCDF) be discharged in wastewaters. Reducing dioxin and furan levels by avoiding the use of elemental chlorine bleaching works to reduce the levels of AOX to safe levels. Secondary treatment, as mandated by the Pulp and Paper Effluent Regulations (Department of Fisheries and Oceans 1992), works to eliminate or reduce many of the AOX compounds, particularly the low molecular weight ones (Leiss 2001).

AOX limits in Canadian provinces vary widely and are as high as 1.5 kg/ADt. These are summarized along with limits from other jurisdictions in Table 2.5. Many of these jurisdictions had recent tightening of the AOX limit, including Ontario in 1998, Quebec in 2001, and British Columbia, effective January 1, 2003. In Alberta, the next change, if any, would likely come with the next approval renewal. The next approval with AOX limits to expire is Alberta-Pacific's, which expires in 2006.

Table 2.5: AOX limit comparison

Jurisdiction	AOX limit (kg/ADt)
Alberta	0.55 to 1.5
Canada	No limit
Ontario	0.8
Quebec	0.8
British Columbia	0.6

2.2.3 International Legislation

Phase 1 of the United States Environmental Protection Agency (USEPA) Cluster Rule was introduced on April 15, 1998. The Cluster Rule is a set of regulations based on best available technology (BAT) for wastewater regulations. An important feature of the “water side” of the regulation includes final wastewater limitations on AOX, as

well as dioxins, furans, and chlorinated phenolics (Vice and Carroll 1998). Although the Cluster Rule is American legislation, it indirectly affects mills in other countries, including Canada. Vice (1998) indicates that the Cluster Rule has been watched closely by Canadian mills as an indicator to future environmental controls, and for possible trade ramifications. She also states that “there has also been discussion and rumour about the potential for American pulp companies to seek a requirement for Canadian competitors to meet the Cluster Rule”. This legislation further emphasizes the importance of AOX reduction. Based on Carey *et al.* (2002) conversions, the USEPA limit is a maximum daily of 1 kg/ADT, and maximum monthly limit of 0.66 kg/ADt. The compliance dates for these limits depend on reissuance of permits. It is expected to be about 2010 before most mills are in compliance (Carey *et al.* 2002).

AOX limits in European countries are varied. The one kraft mill in Germany has a limit of 0.35 kg/ADt and in Austria the limit is 0.5 kg/ADt. In both countries the limit must be met 4 days out of 5. In France the limit is based on an annual average of 1 kg/ADt. Many mill in Sweden and Finland have permit requirements to limit AOX to 1.5 kg/ADt.

Other major pulp producing countries include Japan and Brazil. In Japan, AOX discharges must be below 1.5 kg/ADt. In Brazil, mills are subject to individual discharge permits, similar to Alberta. The limits can range from as low as 0.2 kg/t to a “Swedish style” relationship with regulators where discharges are controlled to low levels and formal regulations are not used extensively (Carey *et al.* 2002).

2.2.4 Using Wastewater Treatment to Meet Discharge Limits

While efforts to meet AOX limits are usually done within the pulping and bleaching process, maximizing wastewater treatment removal may be a cost-effective method of meeting discharge standards. Bryant and Barkley (1991) believe that viable treatment options could ease the capital requirements for bleaching process modifications.

2.3 AOX Removal in Various Wastewater Treatment Systems

Many studies have previously been done to determine the removal efficiency of various wastewater treatment systems on AOX. Treatments such as neutralization, ultraviolet (UV) radiation, ultrafiltration, reverse osmosis, oxidation, and treatment with white rot fungi have been studied. Various secondary (biological) processes such as activated sludge and aerated lagoons have also been studied. The chemical and physical treatments do not compare well with the biological process used at Alberta-Pacific.

Because of the variety of wastewater treatment systems in place it is safe to conclude that no two systems at different kraft pulp mills are exactly alike. This makes overall removal efficiencies of AOX at the Alberta-Pacific mill difficult to compare to overall removal efficiency at other mills. Based on discussions held with Vic Morandini, Senior Process Specialist at Alberta-Pacific, it is generally accepted that the removal efficiency at Al-Pac (approximately 85-90% based on historical testing) is exceptional (Morandini 1999). This is even more remarkable when it is considered that the influent AOX value is measured after neutralization. It is known that neutralization can destroy a large percentage of AOX (Bottger, *et al.* 1987).

2.3.1 Primary Treatment

Brook's (1997) survey of pulp and paper mill wastewater treatment systems showed removal across primary treatment of 20% and 47% at two particular mills. Other studies have also shown that AOX is removed by primary treatment (Webb 1994). Some removal of AOX compounds can be expected with primary sedimentation as many hydrophobic chlorinated organic compounds such as chlorinated dibenzo-p-dioxins (CDDs) and chlorinated dibenzofurans (CDFs) adsorb to suspended solids (McKinnon 1992).

2.3.2 Secondary Treatment

Many removal efficiencies for activated sludge and aerated lagoon treatment systems have been reported. Brook (1997) reported AOX removal from 28% to 69% in aerated lagoons and 30% to 46% in activated sludge. Wilson and Holloran (1991) report 16 to 68% AOX removal in aerated lagoons and 14 to 65% in activated sludge. LaFond (1991) reported ranges of 4 to 52% for aerated lagoons and 22 to 65% for activated sludge.

Typical AOX removal efficiencies can be expected to be within 15 to 50 % for aerated lagoons (Struthridge and McFarlane 1994). H.A. Simons (1992) reports a typical AOX removal efficiency of 35% for an air activated sludge treatment system with a hydraulic retention time of 12 hours.

2.4 Comparison of AOX discharges between Alberta kraft pulp mills

In Alberta, the four kraft pulp mills use diverse technologies within the pulp mill and for wastewater treatment that result in much different discharges of AOX. The Daishowa-Marubeni mill (Peace River) uses mill technology very similar to Alberta-Pacific and also pulps hardwood (aspen) chips for pulp production. The other two kraft mills, Weldwood (Hinton) and Weyerhaeuser (Grande Prairie) pulp softwood chips. Softwood chips have a higher lignin content than hardwood and require more pulping and bleaching chemicals to achieve a pulp of the same brightness. The result is a wastewater of poorer quality. The bleaching technology used also plays a key role in AOX formation. Table 2.6 summarizes the mill technologies and the AOX discharges of the four Alberta kraft pulp mills (refer to section 1.2.1 for explanation of bleaching sequence abbreviations).

Table 2.6: Alberta kraft pulp mill AOX discharge comparison for 2001.

Mill	Hardwood Production	Bleaching Sequence	Wastewater Treatment	AOX (kg/day)	AOX (kg/ADt)
Alberta- Pacific	86%	DE _{OP} D	Activated Sludge	104	0.06
Daishowa- Marubeni	77%	DE _O DD	Aerated Lagoon	181	0.15
Weldwood	0%	DE _{OP} (DE _N D)	Aerated Lagoon	264	0.23
Weyerhaeuser	0%	DE _{OP} DED	Aerated Lagoon	375	0.56

3. OBJECTIVES

Three primary objectives were proposed for this research:

1. Determine where AOX removal is occurring in the wastewater treatment system at Alberta-Pacific Forest Industries;
2. Hypothesize on what is happening to the AOX based on the results; and
3. Understand why the Alberta Pacific wastewater treatment system is performing at such a high level.

4. MATERIALS AND METHODS

4.1 Sample Locations

Testing was conducted to determine an AOX profile across the wastewater treatment system at Alberta Pacific Forest Industries. Sample locations were chosen to separate wastewater treatment unit processes, i.e. primary treatment, equalization/cooling pond, biological treatment, and secondary clarification. Three of the five sample locations were distribution boxes, which provided a convenient location. The location of the distribution boxes being sampled from are shown in Figure 1.4 and are listed in Table 4.1. Other sample locations include the cooling tower pump station and the final wastewater sampling building. The cooling tower pump station represents the wastewater from the equalization/cooling pond and the influent to the bioreactors prior to mixing with the RAS. The final wastewater building is located after secondary clarification but before the head pond. There is no further wastewater treatment after this location and is consider final wastewater. Table 4.1 summarizes the sampling locations.

Table 4.1: Sampling locations

Location	Abbreviation	Description
Distribution Box #1	DB#1	Primary Clarification influent (includes WAS)
Distribution Box #3	DB#3	Primary Clarification effluent— Equalization/Cooling Pond influent
Cooling Tower	CT	Equalization/Cooling Pond effluent— Bioreactor influent
Distribution Box #5	DB#5	Bioreactor effluent—Secondary Clarification influent
Final Sampling Building	PF	Secondary Clarification effluent (final treated wastewater)

Sampling was designed to help determine at which unit process the removal is taking place in the wastewater treatment system.

4.2 Timing of Sample Collection

The design of the sampling regime was to follow a slug through the system. For example, if the estimated retention time in the primary clarifiers was 3 hours at the current flow rates, then the sample time at DB#3 would be 3 hours after the sample time at DB#1. This was done to provide data to evaluate treatment through each unit process, and to have further understanding of relationships of wastewater treatment to hydraulic retention time, influent concentration, and other operating parameters at the time. It was understood that the slug sampling would have inherent limitations based on this study design. This design assumes that the system is a plug flow (such as a pipe), when in reality only the clarifiers are designed to behave that way. The other unit processes (equalization/cooling and bioreactors) have a significant amount of mixing. Even so, it was felt that this design could provide further insight into treatment performance.

4.2.1 Retention Study Methodology

A retention study for each unit process was conducted prior to sampling. The results of this work can be found in section 5. A slug of INTRACID Rhodamine WT liquid, which was purchased from Crompton & Knowles of Quebec, Canada, was used as a dye. The Rhodamine WT liquid is a fluorescent dye that does not change the characteristics of the wastewater but can be measured at very small concentrations using a fluorometer.

For the retention study, one to two litres of Rhodamine WT liquid was dumped at the sample location prior to the unit process. The sample location following the unit process was then sampled regularly and measured for fluorescence. A response curve was generated and used to determine the average retention time of the in the unit process.

4.3 Operating Requirements

It was necessary that the wastewater treatment system and the pulp mill were operating at a steady rate, to minimize any outside influencing factors. This study was done during hardwood pulping only.

4.3.1 Wastewater Treatment System Operations

Because the spill pond is not part of the normal wastewater treatment system operating conditions, it was desirable not to include it within this study. Sampling avoided times when the spill pond was in use. Not in use meant that wastewater was not being diverted to the spill pond, and wastewater was not being brought back into treatment from the spill pond. All other operating conditions were considered “normal”.

4.3.2 Pulp Mill Operations

Data collection was done at times when the pulp mill was running at steady conditions, particularly in the bleach plant where a considerable portion of the wastewater and all of the AOX was generated. Other areas of the mill can have influencing factors, however it was reasonable to assume that if the bleach plant was running steady for a length of time, then the entire mill was running steady to match production. A reasonable operating rate for the bleach plant can be considered to be above 90% of the design rate (1500 ADt/day). This works out to be 1350 ADt/day.

Steady mill operations helped maintain a steady wastewater flow from the mill. When the wastewater flow from the mill was steady over a period, the parshall flume located at the final wastewater building can be used to estimate flows throughout the wastewater treatment system. The other flow meters located within the wastewater treatment system have been determined to be unreliable and/or inaccurate. Minor changes in flow were averaged out over the sampling period.

It was determined during the hydraulic retention study prior to sampling that the hydraulic retention time of the wastewater treatment system was 59 hours at typical flow rates (refer to section 6.1). Therefore, sampling was not done unless the bleach plant had been running at a rate greater than 1350 ADt/day for longer than 59 hours.

During testing the species of wood being pulped was limited to hardwood. Alberta-Pacific pulps hardwood approximately 80% of the time. Softwood pulping runs are done occasionally (about every two months) for about 8 days at a time. Because of this short duration, it would be very difficult to come to any conclusions on efficiencies of the wastewater treatment system. Due to the complete-mix nature of the system, and the acclimation required by the microorganisms in the bioreactors, the system requires time to return to steady state. Sampling following softwood runs was not done until at least one HRT turnover (59 hours) of the wastewater.

4.4 Testing Performed

AOX testing was complemented with an array of lab tests including total organic carbon (TOC), total suspended solids (TSS), chemical oxygen demand (COD), 5-day biochemical oxygen demand (BOD₅), and colour. In the case of AOX and TOC, measurements were taken to indicate differences in the solid phase and the liquid phase of the wastewater. On-line measurement of temperature, pH, and conductivity were collected where available. This additional data helped understand the removal mechanisms taking place. Daily testing of grab samples occurred over the testing period. Composite samples (as mandated by Al-Pac's Operating Approval) were not used. Composite samples (24-hr) were not used since evaluation of results with regards to HRT made such sampling unpractical. Grab sampling also minimized the effect of biodegradation that may have occurred in the sample carboy during the 24-hour composite sampling period.

Each "slug" would provide replicate data of the wastewater treatment system performance under slightly different operating conditions. Sampling and testing

would continue for a period of time until a reasonable amount of data was collected, with time and resource restrictions being considered.

4.5 Analysis Methods

4.5.1 Sample Collection and Storage

Grab samples were collected once per day (see pictures in Appendix F) when operating requirements were met as detailed in section 4.3. Slug sampling was performed as described in section 4.2.

4.5.2 AOX Methodology

AOX was tested in accordance with Reference Method EPS 1/RM/16, developed jointly by Environment Canada and PAPRICAN. This method was developed to provide a standard for comparison across Canada (Environment Canada and PAPRICAN 1992). One of the benefits of the method is that it provides a means to measure AOX in the suspended solids of the sample. To do this, samples were filtered through a polycarbonate membrane filter. The filtrate was then analyzed according to the method (adsorbed onto carbon following by pyrolysis of carbon in AOX analyzer) to determine the AOX in the liquid phase of the sample. The filter and the solids were also pyrolyzed in the AOX analyzer to determine the AOX in the solids portion of the sample. Analyses were performed at the University of Alberta in Edmonton.

Analysis was done with an Euroglas AOX analyzer, using the column adsorption method, at an oven temperature of 950 °C. Sodium sulphite was not added to the sample to react with residual chlorine, under the assumption that no residual chlorine was present since elemental chlorine is not used in Al-Pac's bleaching sequence. Samples were collected in amber glass bottles and acidified to a pH of greater than 1.5 and less than 2.0. The bottle was completely filled with no headspace. Samples were refrigerated until shipped, and then shipped from the millsite to Edmonton in coolers filled with ice packs to keep the sample cool.

4.5.3 COD Methodology

Chemical Oxygen Demand (COD) testing was done according to Hach Reactor Digestion Method (Hach 1992), using a Hach Odyssey DR/2500 spectrophotometer and mercury free COD vials, also supplied by Hach. Analyses were performed at the Alberta-Pacific environmental laboratory.

4.5.4 Organic Carbon Methodology

Organic Carbon was done in accordance with Standard Methods for Examination of Water and Wastewater Method 5310 B (APHA 1998). The instrument used was a Dohrmann Carbon Analyzer DC80, with a furnace temperature of 800 °C. The filter paper used for the separation of solids has a 0.40 micron pore size (Standard Methods indicates 0.45 micron pore size). Analyses were performed at the University of Alberta.

4.5.5 Total Suspended Solids Methodology

Total suspended solids (TSS) was performed in accordance to Standard Methods for Examination of Water and Wastewater method 2540 D (APHA 1998). Analyses were performed at the Alberta-Pacific environmental laboratory.

4.5.6 BOD₅ Methodology

Five day biochemical oxygen demand was done in accordance with Standard Methods for Examination of Water and Wastewater Method 5210 (APHA 1998). Nitrogenous inhibition was not practiced and the samples were unfiltered. Analyses were performed at the Alberta-Pacific environmental laboratory.

4.5.7 Colour Methodology

The colour test procedure will be in accordance PAPTAC standard H.5 (Pulp and Paper Technical Association of Canada 1993), using a Hach Odyssey DR/2500 spectrophotometer. The sample was filtered through a 0.45 micron filter paper and adjusted to a pH of 7.6. The absorbance was measured at 465 nm. Analyses were performed at the Alberta-Pacific environmental laboratory.

5. RESULTS

5.1 Overview

Prior to sampling, a hydraulic retention study was conducted on each unit process in the wastewater treatment system. The retention study was conducted over a 6 month time frame (December 1999 to May 2000). Samples for AOX analyses were then collected over a 10.5 month time frame (September 2001 to August 2002). A total of 20 “slugs” were analyzed. Earlier testing results (May 2001 to August 2001) were discarded due to laboratory difficulties with AOX testing.

5.2 Retention Study

Sampling times at each sample location were determined by using online flow measurements to most closely estimate the retention time through each unit process. The retention times were based on the results of a retention study completed prior to the start of the sampling regime. Table 5.1 summarizes the findings from this study. The following sections provide more details about the results of this study.

Table 5.1: Wastewater treatment system hydraulic retention times.

Process Unit	Influent Flow (m ³ /s)	Hydraulic Retention Time (hours)
Primary Clarification	0.92	3.7
Equalization/Cooling Pond	1.18	18.7
Bioreactors	1.35	20.3
Secondary Clarification	0.98	3.6
Total		46.3

5.2.1 Primary Clarifier Retention Time

A slug input of a fluorescent dye was added to DB#1 at 8:02 a.m. on May 29, 2000. The wastewater was then monitored for fluorescence at DB#3. The following chart (Figure 5.1) shows the response curve of the slug input. Flows during this time period averaged 0.915 m³/s. Based on this flow, the expected retention time of a plug flow

reactor such as the primary clarifier(s) is $19,440 \text{ m}^3 \div 0.92 \text{ m}^3/\text{s} = 354 \text{ min}$ (5 hr and 54 min).

The retention time is defined as the time where 50% of the area under the response curve is enclosed. This occurs at 224 minutes (3 hr and 44 min), as seen on Figure 5.1.

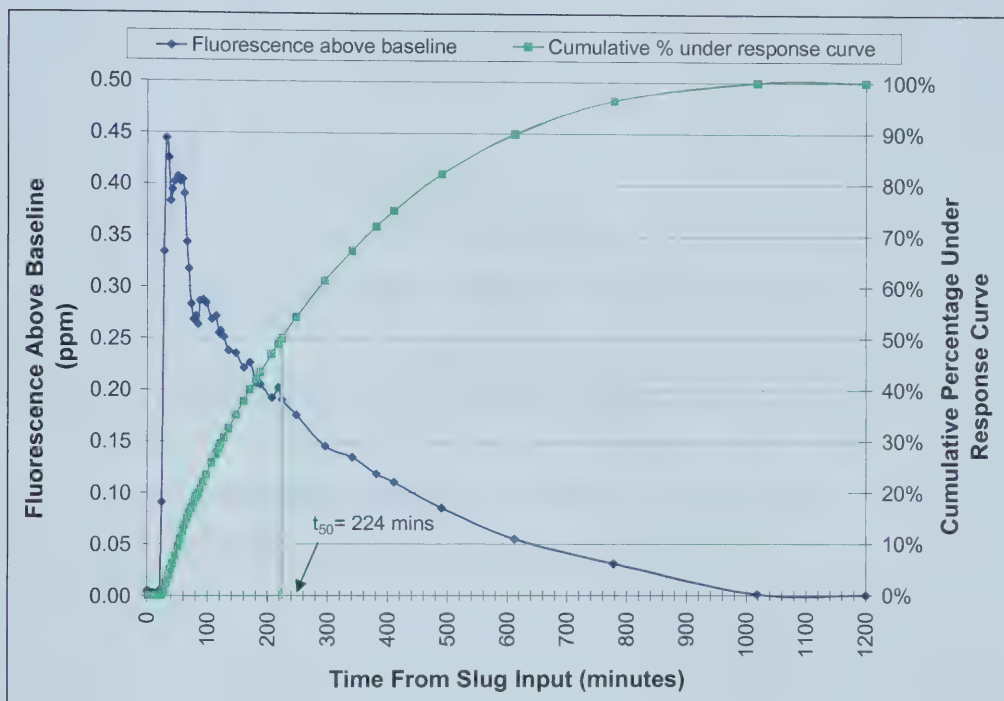


Figure 5.1: Primary clarifier retention response curve

5.2.2 Equalization/Cooling Pond Retention Time

A slug input of a fluorescent dye was added to DB#3 at 7:24 a.m. on March 6, 2000. The wastewater was then monitored for fluorescence at the cooling tower. Actual flow of wastewater during this study averaged $1.18 \text{ m}^3/\text{s}$ and was steady.

The response curve of the dye slug is shown in Figure 5.2. It can be seen from the figure that the average retention time is 18.7 hours.

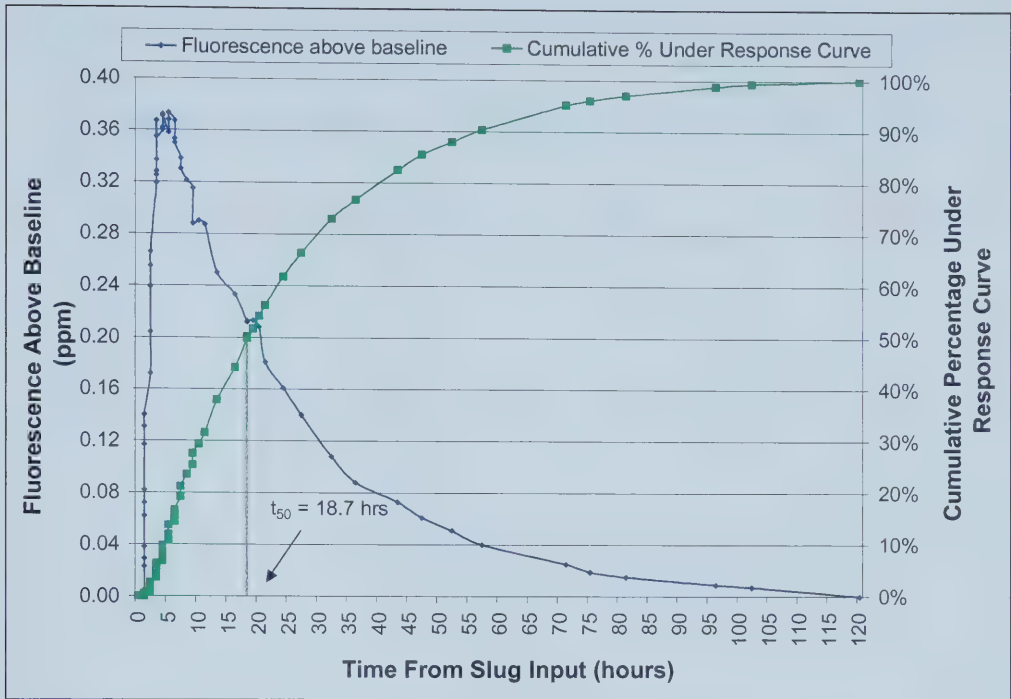


Figure 5.2: Equalization/cooling pond retention response curve

5.2.3 Bioreactor Retention Time

A slug input of a fluorescent dye was added at the cooling tower at 7:20 a.m. on January 19, 2000. The wastewater was then monitored for fluorescence at DB#5. Actual flows during this study were $1.0 \text{ m}^3/\text{s}$ of wastewater and $0.35 \text{ m}^3/\text{s}$ of RAS (see Figure 5.3).

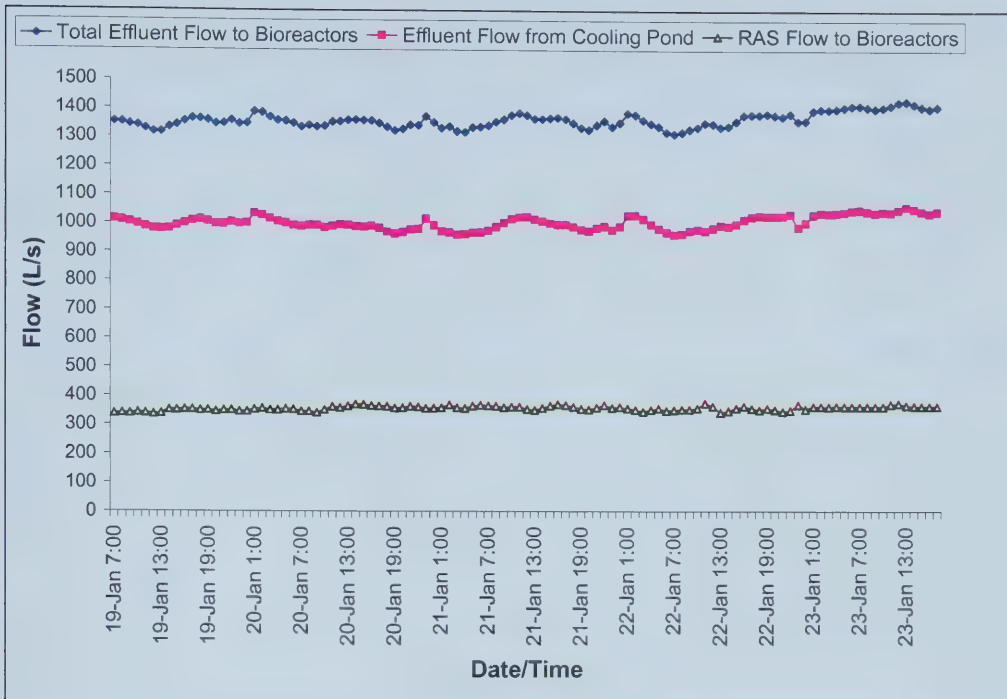


Figure 5.3: Wastewater flow during bioreactor retention study

The response curve of the dye slug is shown in Figure 5.4. It can be seen from the figure that the average retention time is 20.3 hours

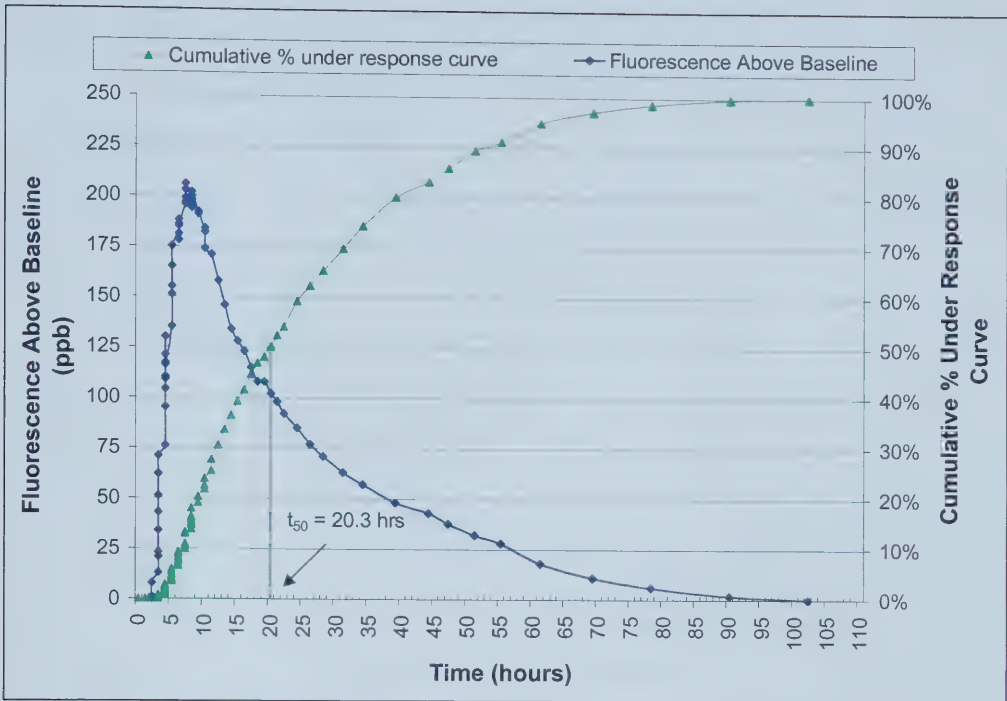


Figure 5.4: Bioreactor retention response curve

5.2.4 Secondary Clarifier Retention Time

A slug input of a fluorescent dye was added to DB#5 at 8:15 a.m. on December 21, 1999. The wastewater was then monitored for fluorescence at the final wastewater building (parshall flume). The following figure (Figure 5.5) shows the response curve of the slug input. The retention time is defined as the time where 50% of the area under the response curve is enclosed. This occurs at 213 minutes (3 hr and 33 min), as seen on Figure 5.5. Flows during this time period were higher than usual, but steady at about $0.98 \text{ m}^3/\text{s}$ (see Figure 5.6).

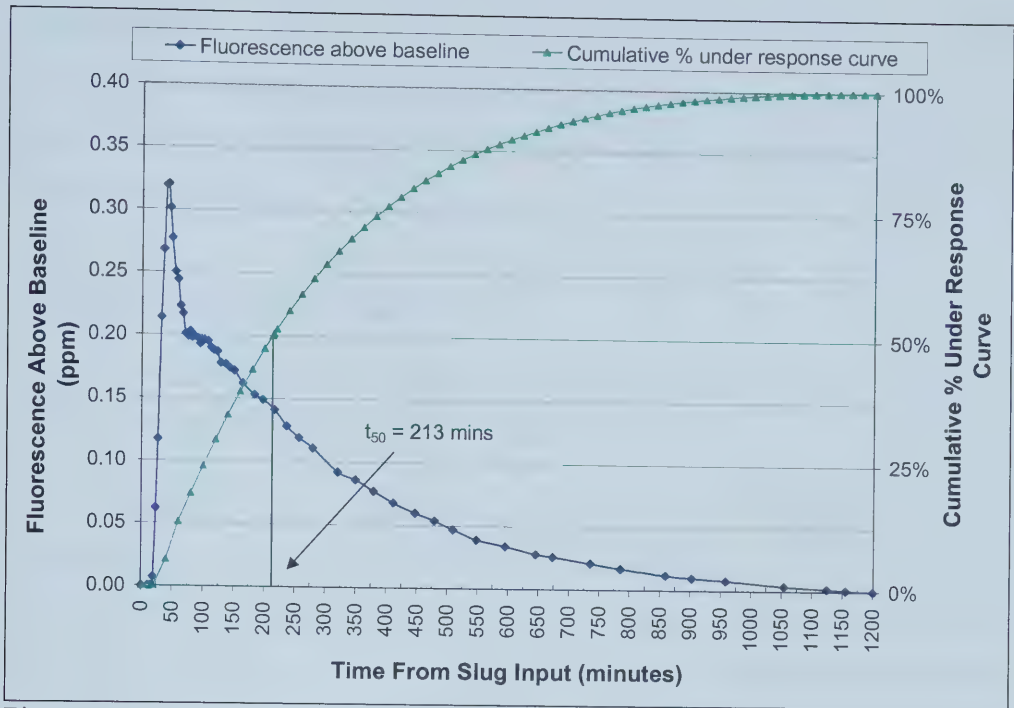


Figure 5.5: Secondary clarifier retention response curve.

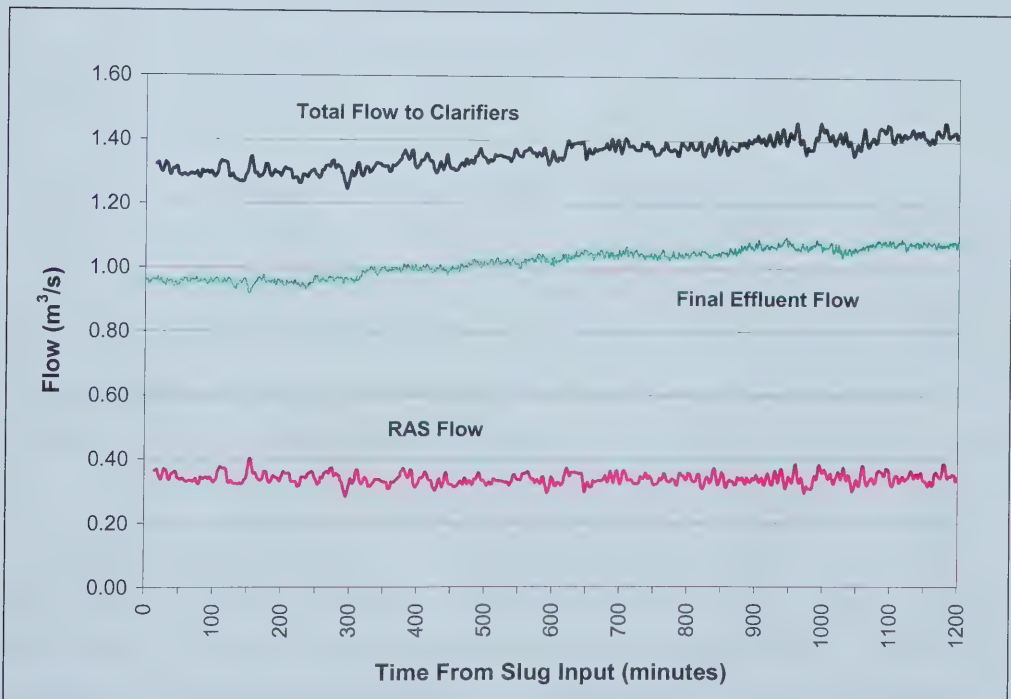


Figure 5.6: Wastewater flow during secondary clarifier retention study.

5.3 Slug Results

Each sample was tested according to the methodology detailed in section 4. A complete compilation of unedited results for each sample location can be found in Appendix B.

5.3.1 Distribution Box #1 Results

Laboratory results from DB#1 samples were generally good. However, a number of discrepancies were found with the BOD₅ test.

For slug 5, a BOD₅ result was not generated. For this sample, 4 replicates were done using dilutions of 1.67% to 13.33 %. This range of dilutions should provide BOD₅ results in the range from approximately 90 to 4300 mg/L, well within the normal range for this sample location. However for this sample, the dissolved oxygen (DO) uptake averaged less than the DO uptake expected due to the seed (average seed DO uptake was 0.87 mg/L, the average DO uptake for this sample was 0.81 mg/L). It is probable that an error in lab procedure resulted in the wastewater sample not being added to the BOD bottles.

The BOD₅ result for slug 9 is also questionable. Although a result of 408 mg/L was determined, there are a number of reasons to reject this test. Firstly, the dilution water oxygen uptakes were 0.66 and 0.45 mg/L. Standard Methods (APHA 1998) says that the dilution water DO uptake should not be more than 0.2 mg/L and preferably not more than 0.1 mg/L, while PAPTAC (Pulp and Paper Technical Association of Canada 1991) says that the BOD of unseeded dilution water should not be greater than 0.5 mg/L. Secondly, final DO readings for this sample were unstable. This means that the DO meter was unable to get a steady reading for a predetermined length of time. This may indicate that there was a problem with the DO meter and/or DO probe for that test. Thirdly, the glucose-glutamic acid standard check was low. Standard Methods (APHA 1998) indicates that the glucose-glutamic acid check should fall within 167.5 to 228.5 mg/L. The check for this sample batch was low at 161.7 mg/L.

Fourthly, it was found that with greater dilution, the BOD was consistently higher for this sample. PAPTAC (Pulp and Paper Technical Association of Canada 1991) states that this is an indicator of something in the sample interfering with the test.

Slug 16 also had a questionable result for BOD₅ at DB#1. For this slug, the blank DO uptake was 0.44 and 0.35 mg/L. However, even more questionable was the wide range of BOD determined for this sample in the replicates. The four replicates ranged from 280 mg/L to 846 mg/L. The higher results were generally with the higher diluted samples, and may indicate interference as discussed above.

The DB#1 BOD₅ values for slugs 5, 9, and 16 were not used in this analysis.

5.3.2 Distribution Box #3 Results

An analysis of the results from DB#3 show that the results of slug 5 stand out among the others. Slug 5 shows increases in all AOX results, all TOC results, and COD across the primary clarifiers. There is also a decrease in colour through this process. These results are opposite of what was found in the other slugs, suggesting that either the DB#1 or DB#3 sample for slug 5 was in error some way (mixed up, contaminated, etc.). For 5 of the measurements (TSS, BOD₅, SOC, AOX liquid, and AOX total) the slug 5 DB#3 results were the maximum of all measurements for this study. For colour, the result was the minimum of all measurements. That this slug was a bad sample was also supported by the fact that the results from two separate labs were questionable and that for online measurements (conductivity, pH, temperature), all results were normal. For these reasons the DB#3 samples for slug 5 were not evaluated in this study.

The BOD for slug 9 DB#3 sample was conducted during the same test as the slug 9 DB#1 sample. This means that the dilution water checks and glucose-glutamic acid checks did not meet quality standards. Final DO readings for the DB#3 sample were also unstable. This result was rejected from the sample set.

5.3.3 Cooling Tower Results

BOD₅ results were also of concern for two of the cooling tower samples. For Slug 5, there appeared to be a problem with the sample batch for that analysis. Both the PAPTAC (Pulp and Paper Technical Association of Canada 1991) and Standard Methods (APHA 1998) procedures indicate that the seed should give a BOD₅ of 0.6 to 1.0 mg/L in the seeded dilution water. For this batch, the seed depletion was much higher than 1.0 mg/L and this resulted in all seeded sample DO uptakes being higher than normal, and often out of range. For the cooling tower sample in this batch, this meant that only one replicate of four met the “take 2, leave 1” rule (oxygen uptake must be at least 2 mg/L and final DO must be at least 1 mg/L). Dilution water blanks were also slightly high for the batch at 0.20 mg/L and 0.20 mg/L. This result was rejected.

For Slug 6, the seed and standard checks were very good. However, there appeared to be a problem with the dilution water with DO uptakes of 0.36 mg/L and 0.50 mg/L. Of most concern with this sample was the wide range of results with the four replicates. Table 5.1 shows these results.

Table 5.2: Results of slug 6 BOD₅ results for cooling tower sample.

Dilution (mL)	BOD₅ (mg/L)
5	1162
10	731
20	589
40	389

These results indicate that there may be some interference with the sample, as discussed earlier.

Slug 7's BOD results also had problems. For this sample the standard check was low (136.2 mg/L). The DO uptake for the cooling tower samples were abnormally low, resulting in BOD₅ of 128 mg/L. This was the lowest result determined for the cooling tower sample in this study. This sample was also rejected from the data set.

The BOD results of slug 11 and 12 were similar to the slug 6 result with decreasing BOD₅ with decreasing dilution (see Table 5.3). The seed depletion was also not within the recommended range of 60 to 100 mg/L (APHA 1998). These results were rejected from the data set.

Table 5.3: Results of slug 11 and slug 12 BOD₅ for the cooling tower sample.

Dilution (mL)	Slug 11 BOD₅ (mg/L)	Slug 12 BOD₅ (mg/L)
5	804*	412*
10	531	254*
20	377	164*
40	248	131

*depletion <2 mg/L

The COD result for slug 2 was unusually high. Further examination revealed that the result was greater than the average plus two standard deviations of the data set (indication of an outlier). Also COD removal efficiency for this slug was -65% through the equalization/cooling pond, and unusually high (88%) through secondary treatment. These removal efficiencies were inconsistent with the other results. This result was rejected.

5.3.4 Distribution Box #5 Results

Since the Distribution Box #5 sample was a mixed liquor sample from the bioreactors, it was in many ways not useful for this study. The BOD₅ and COD tests were performed the same way for these samples as for all the others, in particular, the solids were not filtered from the sample before analysis. Since the solids in the DB#5 sample is made up of the microbes used in the biotreatment, it can be expected that the oxygen demand of such as sample would be high and not indicative of the quality of the wastewater. For this reason, the DB#5 BOD₅ and COD results were not analyzed and dropped from the study.

The testing done to determine the organic carbon content of this sample also produced questionable results due to the high amount of solids. For this reason only the dissolved organic carbon (DOC) result was used in the analysis.

There are a number of results that stand out for the DB#5 TSS. This test is the same test as the mixed liquor suspended solids test (MLSS), a routine test done for operational control by the Water and Effluent Operations Team at Al-Pac. Because it is a test that was done three times a week, and because it is known, based on historical results, that this parameter does not change quickly, it was expected that the test result for this study would be close to the operator tests for the week. This was not the case for Slug 1, 2, and 9. For these tests, the results were not near the operator results, and they were outside of what would be considered reasonable results for the operating conditions at the time. For these reasons, these three results were replaced with the results from the nearest operator test for that time.

5.3.5 Parshall Flume Results

The parshall flume sampling location is the same sample location used for compliance monitoring by Alberta Pacific. Al-Pac's approval requires much of the same monitoring that was done for this study. Refer to Appendix A for a summary of these requirements. As a extra check for testing accuracy, the results from this study were compared to results determined for compliance monitoring.

The TSS grab samples for this study were generally very close to the 24-hour composite sample results for the same day. However, for slug 7, a reported TSS of 3 mg/L did not compare well with the 24-hr composite result of 37 mg/L on the same day (a TSS as low as 3 mg/L is not be considered normal, regardless). The value of 37 mg/L was used as a better estimate of actual TSS for the sample.

Slug 8 had the maximum (or minimum) measurements for a number of parameters of all slugs in this study. This slug was sampled only 6 days following a softwood run (approximately 141 hours after 100% hardwood in the bleachplant). This is equivalent

to approximately 2.4 times the hydraulic retention time of the system, and within our study plan as outlined in section 4.3.2. However, it is believed that due to the cold weather at the time (-20°C to -30°C) combined with the upset from softwood wastewater, the secondary treatment system did not recover as quickly as it normally does from the change in influent wastewater characteristics. These results are believed to be legitimate, though not entirely indicative of normal hardwood operations.

5.3.6 Results-Overview of Edited Data

A compilation of edited results for each sample location can be found in Appendix C.

6. DISCUSSION

6.1 Retention Study Results

A summary the expected hydraulic retention times can be seen in Table 6.1.

Discussion on each process unit and an explanation of “effective volume” can be found in the following sections.

Table 6.1: Expected wastewater treatment system hydraulic retention times based on retention study

Process Unit	Effective Volume (m ³)	Typical Influent Flow (m ³ /s)	Expected Retention Time (hours)
Primary Clarification	12,298	0.83	4.1
Equalization/Cooling Pond	79,438	0.83	26.5
Bioreactors	98,658	1.15	23.8
Secondary Clarification	12,461	0.83	4.2
Total			58.6

The total HRT for the system as determined by the retention study is 58.6 hours at typical flows. The design of the system was 73.6 hours (refer to section 1.2.2.2) at slightly lower wastewater flows and higher recycled activated sludge flows. The retention time for the entire system seems to be reasonable, but not exceptional. It can be concluded that the HRT for the system is satisfactory, but that the HRT performance cannot explain the exceptional treatment performance of the system.

6.1.1 Primary Clarifier Hydraulic Retention Time

The hydraulic retention time of wastewater in the primary clarifiers was determined to be 224 minutes at a flow of 0.92 m³/s. Since the primary clarifiers are designed as a plug flow reactor, the theoretical HRT at this flow should be is $19,440 \text{ m}^3 \div 0.92 \text{ m}^3/\text{s} = 354 \text{ min}$. Thus, the actual HRT was shown to be only 63% of the theoretical HRT. This indicates that some short-circuiting is occurring through the primary clarifiers.

Based on the results, an effective volume was calculated and used to better estimate of HRT at a given flow. The effective volume was calculated as $0.92 \text{ m}^3/\text{s} \times 224 \text{ min} = 12,298 \text{ m}^3$ (6149 m^3 for each clarifier). At the typical flow of $0.83 \text{ m}^3/\text{s}$, the expected HRT is then $12,298 \text{ m}^3 \div 0.83 \text{ m}^3/\text{s} = 246 \text{ min}$. The HRT through the primary clarifiers can be estimated for any flow by using the effective volume in the above calculation. The use of an “effective” volume provides an estimate of hydraulic retention times at varying flows. While this tool is not perfect (it may be expected that the “effective” volume would differ depending on flow volume), it provides a rough estimate to evaluate the effect of hydraulic retention time on treatment performance.

6.1.2 Equalization/Cooling Pond Hydraulic Retention Time

The equalization pond is, in theory, a perfect CFSTR (continuous flow stirred-tank reactor). Figure 6.1 shows the theoretical response of the equalization pond if it behaves as a perfect CFSTR and if it behaves as perfect plug flow reactor (based on flow of $1.2 \text{ m}^3/\text{s}$).

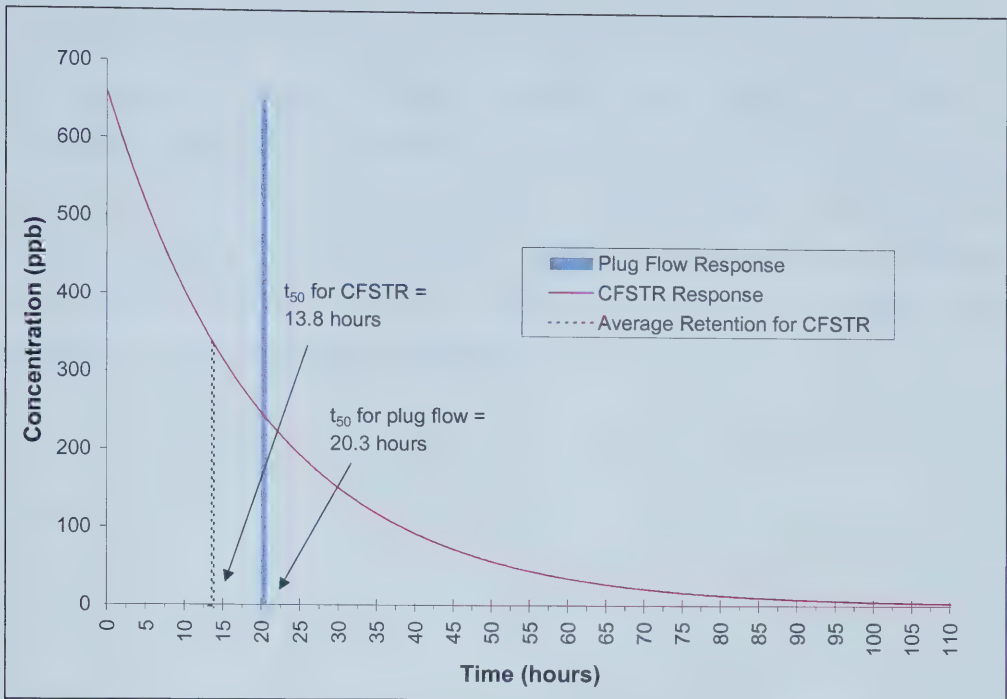


Figure 6.1: Theoretical HRT for a CFSTR and plug flow reactor the same volume as the equalization/cooling pond

The results of the calculations for retention times are shown on the chart (Figure 6.1). It can be seen from the chart that the theoretical HRT for the plug flow is 20.3 hours, whereas for the CFSTR it is only 13.8 hours. The HRT determined in the study showed a HRT of 18.7 hours (at the study flow of $1.2 \text{ m}^3/\text{s}$). This was not surprising, as most CFSTR's will in reality never function as "perfect" CFSTR's, but will behave somewhere between a perfect CFSTR and a perfect plug flow reactor.

Based on the results, an effective volume was calculated and used to better estimate of HRT at a given flow. The effective volume was calculated as $1.2 \text{ m}^3/\text{s} \times 18.7 \text{ hr} = 79,438 \text{ m}^3$. At the typical flow of $0.83 \text{ m}^3/\text{s}$, the expected HRT is then $79,438 \text{ m}^3 \div 0.83 \text{ m}^3/\text{s} = 26.5 \text{ hours}$. The HRT through the equalization/cooling pond can be estimated for any flow by using the effective volume in the above calculation.

6.1.3 Bioreactor Hydraulic Retention Time

Each bioreactors is actually 5 CFSTR's (continuous flow stirred-tank reactors) in a series, with 4 smaller cells, followed by a larger 5th cell (refer to Figure 1.4). This design is done to increase the retention time of mixed reactors towards the longer retention of a plug flow design, while still providing adequate mixing. Figure 6.2 shows the theoretical response of the two types of reactors with the equivalent volume as the bioreactors (based on flow during study of $1.4 \text{ m}^3/\text{s}$).

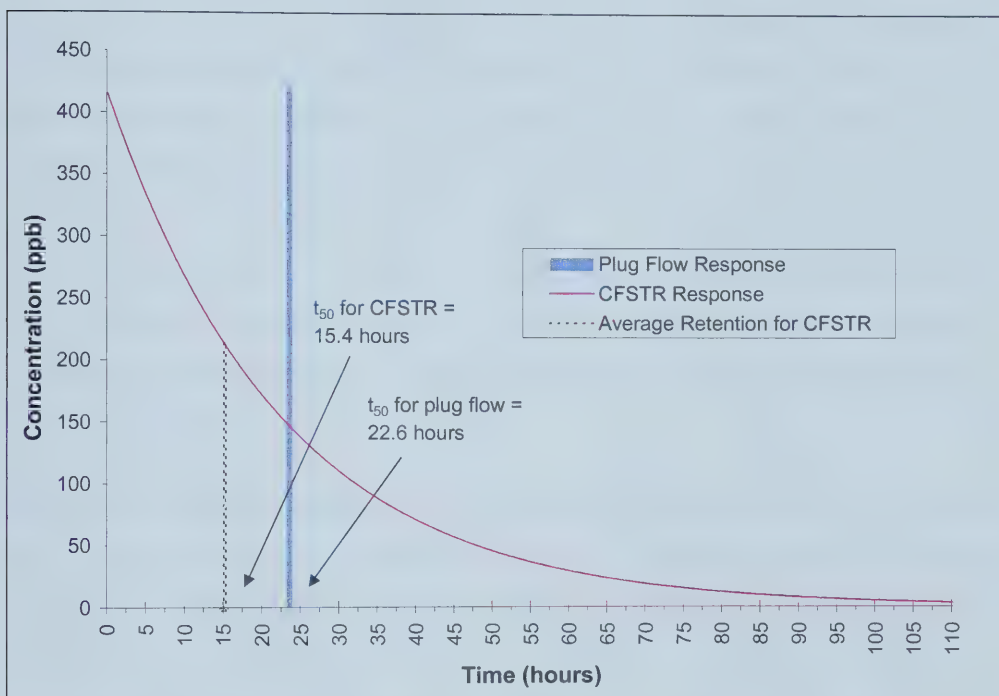


Figure 6.2: Theoretical HRT for a CFSTR and plug flow reactor the same volume as the bioreactors

It can be seen from the chart that the theoretical retention time for the plug flow is 22.6 hours, whereas for the CFSTR it is only 15.4 hours. The actual HRT determined for the bioreactors was 20.3 hours. This is very close to the theoretical HRT, indicating that the bioreactors have adequate retention.

Based on the results, an effective volume was calculated and used to better estimate HRT at any given flow. The effective volume was calculated as $1.4 \text{ m}^3/\text{s} \times 20.3 \text{ hr} = 98,658 \text{ m}^3$. At the typical flow of $1.2 \text{ m}^3/\text{s}$, the expected HRT is then $98,658 \text{ m}^3 \div 1.15 \text{ m}^3/\text{s} = 23.8 \text{ hours}$. The HRT through the bioreactors can be estimated for any flow by using the effective volume in the above calculation.

6.1.4 Secondary Clarifier Hydraulic Retention Time

The hydraulic retention time of the secondary clarifiers was determined to be similar to the primary clarifiers. The HRT of wastewater in the secondary clarifiers was determined to be 213 minutes at a flow of $0.98 \text{ m}^3/\text{s}$. The secondary clarifiers are designed similar to the primary clarifiers, only larger in size. This means that they should, in theory, behave as a plug flow reactor. The theoretical HRT at the study flow should be $25,600 \text{ m}^3 \div 0.98 \text{ m}^3/\text{s} = 438 \text{ minutes}$. The actual HRT was shown to be only 49% of the theoretical HRT. This indicates that some short-circuiting is occurring through the secondary clarifiers, similar to the short circuiting occurring in the primary clarifiers.

Based on the results, an effective volume was calculated and used to better estimate of HRT at any given flow. The effective volume was calculated as $0.98 \text{ m}^3/\text{s} \times 213 \text{ min} = 12,461 \text{ m}^3$, or 6230 m^3 for each clarifier. At the typical flow of $0.83 \text{ m}^3/\text{s}$, the expected HRT is then $12,461 \text{ m}^3 \div 0.83 \text{ m}^3/\text{s} = 249 \text{ min}$. The HRT through the secondary clarifiers can be estimated for any flow by using the effective volume in the above calculation.

6.2 Location of AOX Removal

6.2.1 Removal Summary

A summary of all AOX testing can be found in Table 6.2. A summary of removal efficiencies can be found in Table 6.3.

Table 6.2: AOX result summary

Sample Location	Solid AOX (mg/L)	Dissolved AOX (mg/L)	Total AOX (mg/L)
Distribution Box #1	0.8	8.0	8.8
Distribution Box #3	0.4	4.6	5.0
Cooling Tower	0.6	2.8	3.3
Distribution Box #5	7.9	0.7	8.7
Parshall Flume	0.1	0.9	1.0

Table 6.3: AOX removal summary

Unit Process	Solid AOX Removal (%)	Dissolved AOX Removal (%)	Total AOX Removal (%)
Primary Clarification	53	42	43
Equalization/Cooling	-26	37	32
Bioreactors	-1441	76	-148
Secondary Clarification	98	-27	88
Secondary Treatment*	76	69	71
Total System	88	89	88

*Includes Bioreactors and Secondary Clarification

AOX attributed to suspended solids decreased significantly through the clarification stages, as would be expected. A slight increase occurred through the equalization/cooling pond and a large increase occurred through the bioreactors. The increase through the bioreactors is attributed to the large increase in solids because of the addition of RAS. This is not an indication of system performance since the addition of RAS occurs after the cooling tower sample location.

Soluble AOX decreased at each stage except secondary clarification, where an average increase of 0.7 mg/L to 0.9 mg/L was noticed. This will be discussed further in section 6.2.4.

Overall AOX removal for the system showed an average decrease from 8.8 mg/L to 1.0 mg/L, a removal efficiency of 88% (86% to 90% at 95% confidence).

6.2.2 Primary Clarification Removal

AOX removal occurred in both the solid phase and liquid phase during primary clarification. Removal of AOX in the solid phase can be expected since the main purpose of the primary clarifier is to remove solids. Average TSS removal through this process was 84%. Since the removal of AOX contained in solids was only 53%, it suggests that AOX is contained in solids that are harder to settle (and thus harder to remove during the clarification process). Solids entering the primary clarifiers are predominantly made up of reject fibre from the mill, water treatment filter backwash, limemud, general sewer solids, and waste activated sludge. Of these, the most difficult to settle is likely WAS, so it is possible a large portion of the AOX in the solid phase entering DB#3 is in the activated sludge being wasted from secondary treatment.

The results show the removal of suspended solids is a contributor to the reduction in AOX. Since the results of this study clearly show that AOX is present in the solid phase, this is no surprise. This is consistent with previous works (Struthridge and McFarlane 1994, and Wigilus, *et al.* 1988).

It is very surprising that there is 42% average reduction of the AOX in the liquid phase. The retention time in this process is short (2.5 to 5 hours in this study) and no removal of soluble organic material is intended to take place during primary clarification. Overall, of the 7.8 mg/L of total AOX removed (on average) for the total wastewater treatment system, 3.8 mg/L, or 49%, of the total removal occurs in the primary clarifiers.

There is, however, a number of ways that AOX reduction in the liquid phase could have occurred. These mechanisms may include: neutralization, adsorption, biological degradation, and volatilization.

Neutralization has shown to significantly reduce AOX (Bottger, *et al.* 1991, H.A. Simons, 1992). alkaline hydrolysis appeared to be the dominant reaction, although the

precipitation of lignin also contributed to AOX removal. Due to the variability of acidity entering the primary clarifiers at Al-Pac, there may be AOX reduction occurring due to pH changes. In practice, a significant amount of caustic (NaOH) is added at the neutralization chamber prior to distribution box #1. The entire breakdown of AOX due to this caustic addition may not be seen until after the DB#1 sample point. The time that it takes the wastewater to reach DB#1 after caustic addition is in a typical range of 5 to 10 minutes. This may not be long enough for all chemical reactions resulting from the caustic addition to occur.

Previous studies have shown that initial adsorption of chlorinated organic material onto solids suspended in the wastewater can be responsible for much of the AOX removal (Struthridge and McFarlane 1994). Comparison of the AOX content in the solids entering the clarifiers against the AOX content of the solids exiting the clarifiers may support this. The ratio of the AOX concentration to the TSS concentration is 0.0013 at DB#1 and 0.0041 at DB#3, indicating that the concentration of halogens in the solids triples from DB#1 to DB#3. It is impossible to determine exactly what portion of this effect is from adsorption. As mentioned above, this effect may be partially or entirely due to the ease of settleability of non-halogenated solids. Biological degradation and absorption by carried over activated sludge (WAS) may also be contributing.

If adsorption onto solids is a contributor to soluble AOX removal, it can be expected that there would be opportunity for more adsorption with higher influent TSS. Greater absorption may also occur if the retention time is longer. The data obtained in this study does not support this, however. Figure 6.3 shows the comparison between influent (DB#1) TSS and soluble AOX removal through the primary clarifiers. Figure 6.4 shows the comparison between the HRT in the primary clarifiers and soluble AOX removal. These figures illustrate that no significant relationships exist between these measurements.

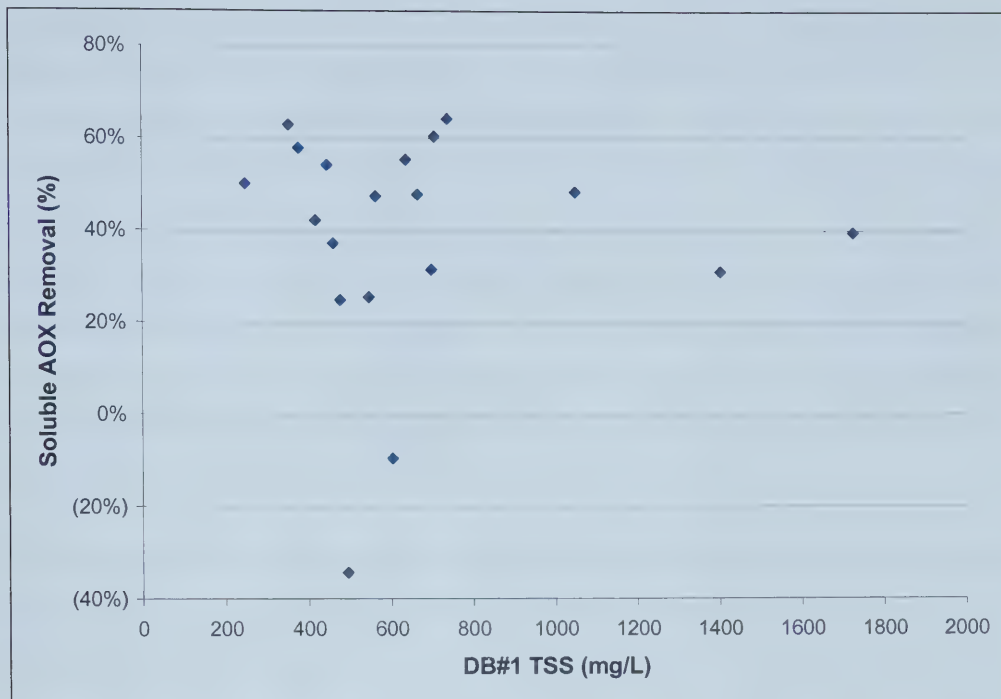


Figure 6.3: Relationship between influent TSS and soluble AOX removal.

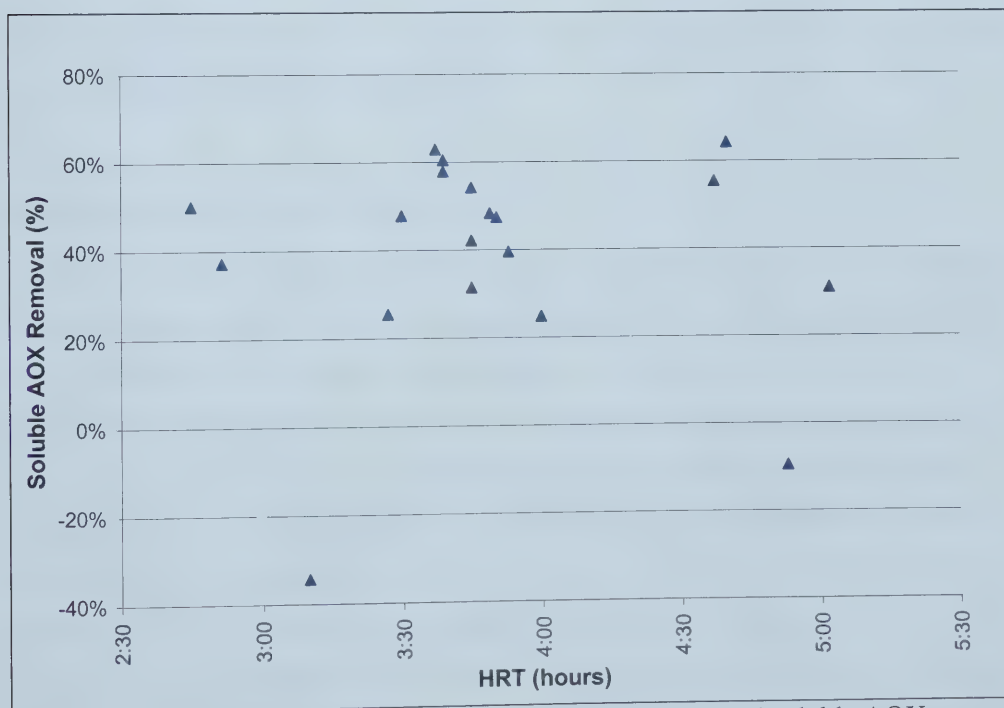


Figure 6.4: Relationship between HRT in primary clarifiers and soluble AOX removal

As mentioned earlier, the return of activated sludge to the start of the wastewater treatment system is not widely practiced. While one of the main reasons for this operating strategy is to minimize sludge handling costs, it may be a key reason for the effectiveness of the wastewater treatment system at Al-Pac. The presence of activated sludge bacteria from the beginning of the wastewater treatment process may allow for more efficient degradation of larger organic molecules, by allowing more time for the break down to take place. Also, because of the high oxygen demand of the wastewater at this point, there may be anoxic conditions present where some anaerobic microbial degradation will also take place. Häggblom and Salkinoja-Salonen (1991) found that anaerobic bacteria can remove a significant amount of AOX.

Volatization of AOX compounds is possible but not likely to be very significant at this stage in the process. While the higher temperatures increases the likelihood of volatization, there is no catalyst (such as aeration) occurring to help this process. As a result, volatization was expected to be low.

Relationships between AOX removal in the primary clarifiers and removal of the other measured parameters were not seen.

6.2.3 Equalization/Cooling Pond Removal

AOX removal in the equalization/cooling stage was similar to the primary clarification stage for soluble AOX (39% and 40%, respectively). Since solids carryover from the primary clarifiers will contain activated sludge, and aeration occurs in the equalization/ cooling pond, the main mechanisms for the removal are thought to be aerobic biological degradation and adsorption, similar to what is occurring in the primary clarifiers, as discussed above. It could be expected that much better removal of soluble AOX would take place here as compared to primary clarification since the retention time of this unit process is almost 7 times greater than primary clarification (average of 3:48 and 25:48). This was not the case based on the results of this study.

An explanation may be that the degradation of easy to degrade AOX has already occurred in the primary clarifiers.

Volatization could be a contributing factor due to the aeration of the wastewater in this stage.

Removal of AOX in the solid phase did not occur, but actually increased by 22% through the equalization/cooling pond (0.41 mg/L at DB#3 and 0.50 mg/L at CT). The difference may be attributed to the variance in the system due to mixing and to the sampling and measurement variance. However, biological consumption and adsorption onto suspended solids would reduce the AOX in the liquid phase while increasing it in the solid phase. This is supported by these results.

Relationships between AOX removal in the equalization/cooling pond and removal of the other measured parameters were not seen.

6.2.4 Bioreactor and Secondary Clarification Removal

The addition of RAS to the front of the bioreactors makes analysis of AOX removal in the bioreactors and secondary clarifiers difficult if looking at each unit process individually. Secondary treatment is commonly referred to in the industry as both the aeration basin (bioreactors) and sedimentation tank (clarifiers) when discussing activated sludge systems. For this reason, these two unit processes will be looked at collectively.

AOX removal through secondary treatment was found to be 71% (68% to 74% at 95% confidence). This is higher than any previously published removal efficiency for similar biological treatment systems. Gergov *et al.* (1988) found that activated sludge can remove up to 65% of AOX, the highest of all published reports.

An average increase of soluble AOX from 0.7 to 0.9 mg/L (or 27%) occurred during secondary clarification (this was not due to a small number of samples skewing the

average, as a 7 to 30 percent increase was noticed in 14 of the 20 slugs sampled). The characteristics of the wastewater from distribution box #5 and the parshall flume sample locations are almost identical except for the concentration of activated sludge (averages of 3900 mg/L for DB#5 and 18 mg/L for PF during this study). It is possible that further biological degradation is taking place in the sample between the sample time and analysis time, even with sample preservation to a low pH. The high concentration of microbes in the DB#5 sample allows for this to happen at a much higher rate relative to the PF sample. Thus, the increase in soluble AOX from DB#5 to PF is most likely attributed to sample handling methods. Further work needs to be done to confirm this.

One of the more unique characteristics of the activated sludge system at Al-Pac is the sludge age. The typical sludge age at Al-Pac is 50 to 70 days (50 to 60 days during this study), based on calculations that include the clarifier volume. It has been shown that higher AOX removals can be found with higher sludge ages (Rempel, *et al.* 1992; Ataberk and Gökçay 1997). Rempel *et al.* (1992) postulated that at longer sludge retention times, food limiting conditions occur, and that a microbial population acclimated to the degradation of more difficult to degrade compounds, such as chlorinated organic compounds, would develop. It was very possible that this acclimation was occurring at Al-Pac.

An atypical sludge age is not the only unique operating feature of the Al-Pac secondary treatment system. It should be noted that nutrient addition is not practiced at all. While nutrients were added for the start-up of the system in the early 1990's, there has been no addition of nitrogen or phosphorus since. The usual nutrient requirements for a system of this type ($BOD_5 : P : N = 100 : 5 : 1$) are neither monitored nor maintained. The source of nitrogen is mainly from human waste via the general sewer. Phosphorus is used in the mill process as a treatment chemical for boiler feedwater, and will eventually become part of the mill wastewater stream. These sources seem to be able to provide enough nutrients to enable the system to perform at a very high level while maintaining final effluent nutrient levels very low.

It has also been observed that higher AOX removal rates occur with higher influent concentrations for various treatment systems (Bryant *et al.* 1992; Roy-Arcand and Archibald 1995). This effect was not seen through the secondary treatment system during this study. Figure 6.5 illustrates this relationship.

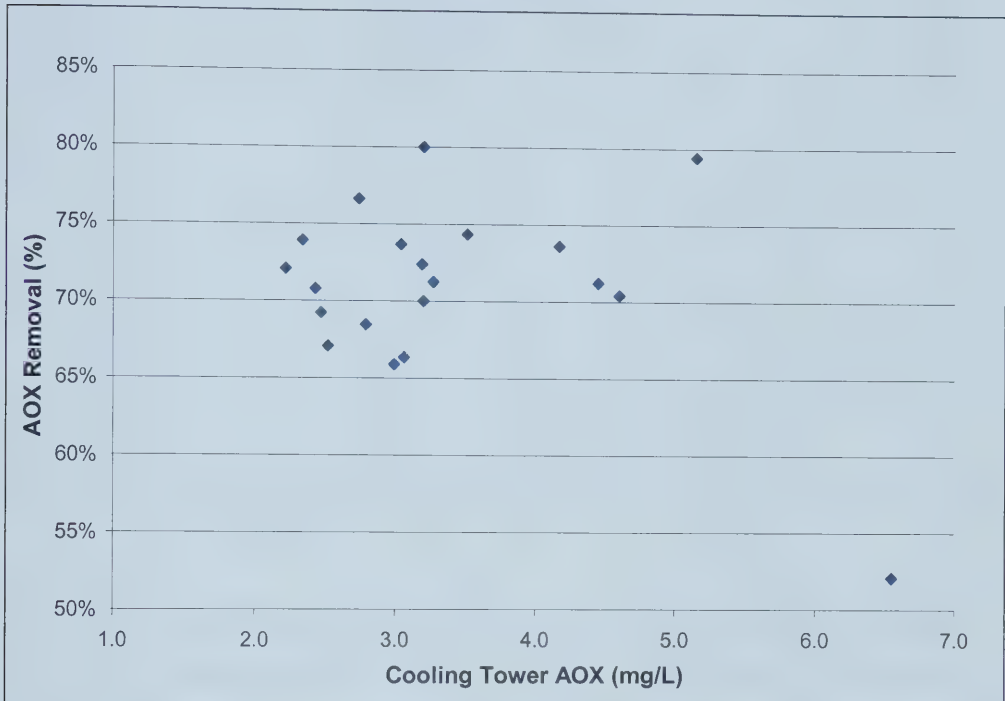


Figure 6.5: Effect of secondary treatment influent concentration on removal efficiency.

It was expected that there would be a high correlation between the removal of AOX in the secondary treatment system with the removal of other organic constituents as measured by TOC, COD, and BOD₅. The results of this study showed a poor relationship between the removal efficiency of AOX and the removal efficiency of each of these measures. Figure 6.6 illustrates these relationships.

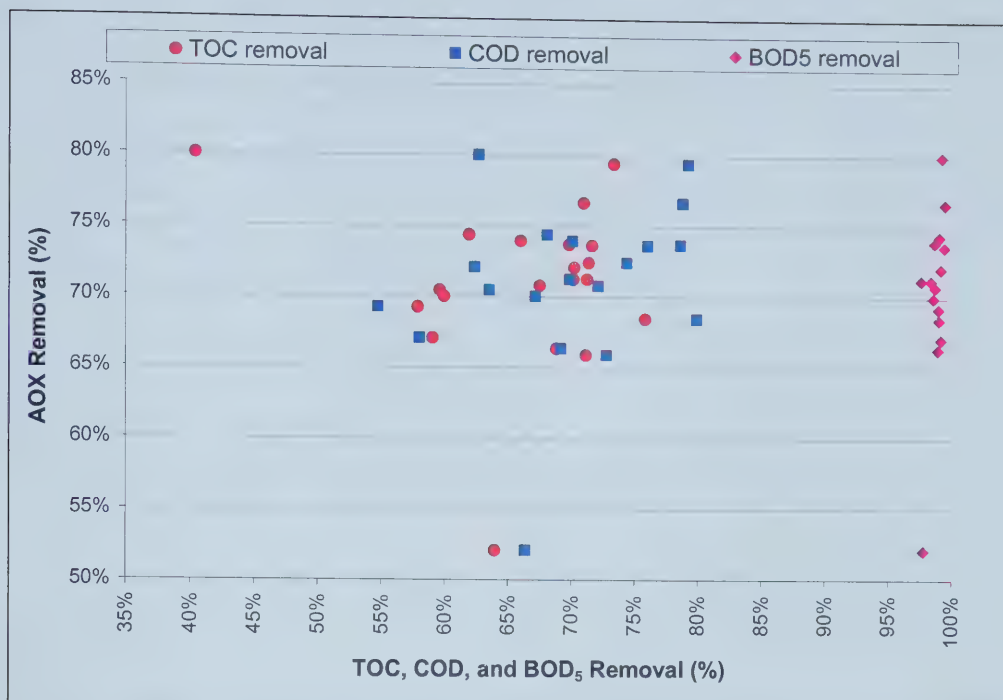


Figure 6.6: Secondary treatment total AOX removal efficiencies versus other organic removal efficiencies.

It was also expected that there would be a strong correlation between the efficiency of colour removal and the efficiency of AOX removal. In kraft pulp mill wastewater, colour is largely a measure of the amount of dissolved lignin, which is a large organic molecule. The AOX entering the secondary treatment process is also primarily made up of large organic molecules (as mentioned earlier, approximately 80% of AOX is >1000 dalton; it is further hypothesized that the smaller AOX constituents are broken down and removed in the earlier stages of wastewater treatment). Thus, it was expected that the ability for the activated sludge process to breakdown these components (colour and AOX) would be roughly equal. This was not the case, as illustrated in Figure 6.7. For this comparison, colour removal is compared to the removal of soluble AOX, given that the colour test is done on a filtered sample.

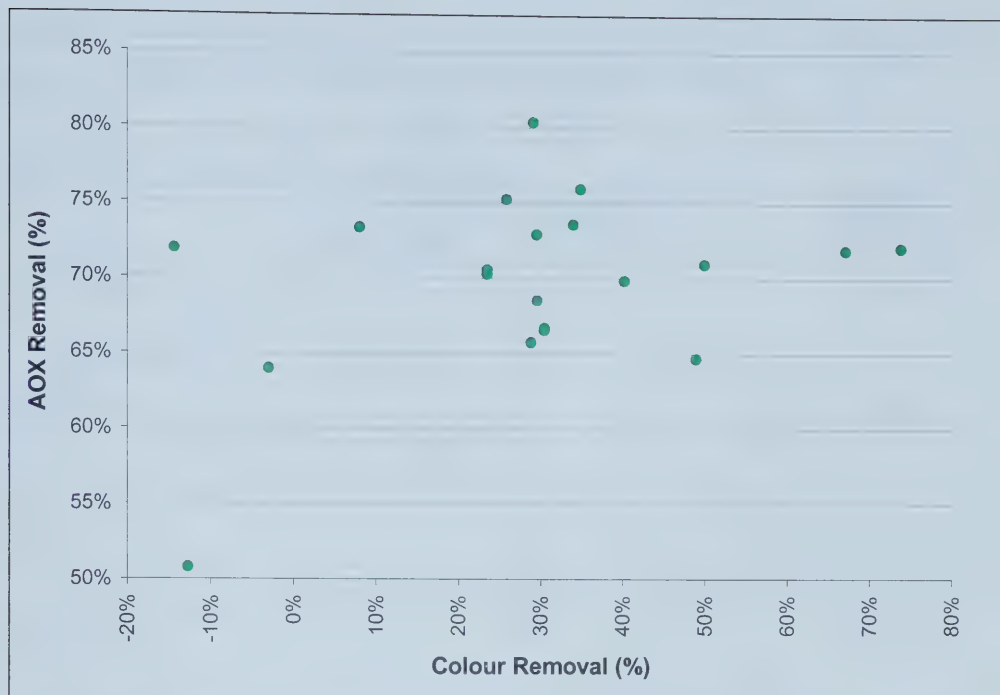


Figure 6.7: Secondary treatment colour removal relation with soluble AOX removal.

Relationships between AOX removal in the secondary treatment process and removal of the other measured parameters were not seen. This includes comparisons made to data related to bioreactor performance and secondary clarification performance individually.

6.2.5 Total System Performance

The wastewater treatment system at Al-Pac proved to perform admirably with regards to AOX removal. This is particularly notable considering there has been no efforts to maximize the efficiency of AOX removal from the Al-Pac Water and Effluent Operations Team. Also, the reduction of AOX through the wastewater treatment system has not been at the expense of other parameter reduction as measured in this study. The removal of COD and TOC were both greater than 80% for the system, and the removal of BOD₅ was exceptional at 99.1%. Table 6.4 summarizes the removal

efficiency of each parameter measured in this study. Total removal efficiencies are calculated as the averages of the removal efficiency for each slug.

Table 6.4: Summary of system performance

	Sample Location					Total Removal Efficiency
	DB#1	DB#3	CT	DB#5	PF	
TSS (mg/L)						96%
<i>mean</i>	647	97	94	4020	20	
<i>standard deviation</i>	375	37	28	703	8	
BOD ₅ (mg/L)						99%
<i>mean</i>	350	311	264	<i>N/A</i>	3.0	
<i>standard deviation</i>	91	72	68	<i>N/A</i>	1.3	
COD (mg/L)						81%
<i>mean</i>	1076	783	658	<i>N/A</i>	195	
<i>standard deviation</i>	229	119	123	<i>N/A</i>	46	
Colour (CU)						16%
<i>mean</i>	292	353	317	237	231	
<i>standard deviation</i>	86	145	98	106	67	
SOC (mg/L)						85%
<i>mean</i>	96	39	50	<i>N/A</i>	12	
<i>standard deviation</i>	29	17	23	<i>N/A</i>	11	
DOC (mg/L)						78%
<i>mean</i>	240	210	143	108	54	
<i>standard deviation</i>	29	31	29	25	18	
TOC (mg/L)						80%
<i>mean</i>	336	250	193	<i>N/A</i>	65	
<i>standard deviation</i>	46	43	39	<i>N/A</i>	12	
AOX solid (mg/L)						85%
<i>mean</i>	0.8	0.4	0.6	7.9	0.1	
<i>standard deviation</i>	0.5	0.3	0.3	2.5	0.1	
AOX liquid (mg/L)						89%
<i>mean</i>	8.0	4.6	2.8	0.7	0.9	
<i>standard deviation</i>	2.5	1.2	0.8	0.4	0.4	
AOX Total (mg/L)						88%
<i>mean</i>	8.8	5.0	3.3	8.7	1.0	
<i>standard deviation</i>	2.7	1.3	1.1	2.3	0.5	

The removal of colour was low, averaging only 16% for this study. In fact, the colour actually increased in 4 of the 20 slugs sampled. There are a couple of explanations that may explain this. The first explanation is the variability of the wastewater at the DB#1 sample location. That is, the timing of the initial sample was critical if the wastewater colour was changing (the initial DB#1 sample may have been collected at the “valleys” more than the “peaks”). The other explanation, which is supported by the results of this study, is that there is a colour increase occurring in the system, and in particular, during the first few hours while the caustic addition solubilizes any lignin that had precipitated out prior to neutralization. The solubilization of lignin increases the colour of the wastewater. Thus, the same effect that may be reducing AOX in the primary clarifiers may also be contributing to an increase in colour. Table 6.5 shows the average measurement of colour at each sample location compared with removal efficiencies.

Table 6.5: Colour removal

	Average colour measurement (mg/L)	Removal from previous stage (%)
Distribution Box #1	292	
Distribution Box #3	353	-21
Cooling Tower	317	10
Distribution Box #5	237	25
Parshall Flume	231	3

7. CONCLUSIONS

This study revealed many efficiencies of the wastewater treatment system at the Alberta Pacific Forest Industries pulp mill, including:

- Almost 50% of AOX removal is occurring in the first few hours of the treatment system, during the primary clarification stage.
- The equalization/cooling process is not only providing its design function of reducing the temperature and homogenizing the wastewater in preparation for secondary treatment, but it is also contributing significantly to wastewater treatment, including AOX reduction.
- Neutralization of mill wastewater by caustic addition may be a major contributor to the removal of organic compounds in the primary clarifiers.
- Waste activated sludge recycle may be a major factor to the removal of organic compounds in the primary treatment processes.
- An older sludge age may be a key reason for the performance of the extended aeration activated sludge secondary treatment process.
- The activated sludge system at Alberta-Pacific Forest Industries is performing at a very high level by measurement of AOX and BOD₅ removal (88% and 99%, respectively).

8. RECOMMENDATIONS

This results of this research have exposed many possibilities to explain the high performance of the Alberta-Pacific pulp mill wastewater treatment system. For further understanding of removal mechanisms and optimal operating conditions, the following is a list of recommendations for further study:

- The effect of caustic addition for pH control prior to primary clarification requires more research to understand the effect on wastewater treatment. Caustic addition should be compared to other neutralization methods.
- The performance of the system should be evaluated to determine the effect of activated sludge wasting to the wastewater stream prior to the primary clarifiers.
- The performance of the activated sludge system should be evaluated at differing sludge ages to determine the effect that an older sludge age has on removal of AOX and BOD. A bench scale trial would be beneficial to manage the many uncontrollable features of the system.
- The system should be evaluated to determine the current source of nutrients and the form in which they enter the system.
- The system should be evaluated to determine performance at varying concentrations of nutrients.
- AOX sampling and storage requirements should be studied to determine the effect of total suspended solids (TSS) concentration and sample storage time on AOX results for secondary treatment samples, recognizing that TSS in secondary samples is made up of activated sludge (microbes).

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10. APPENDIX A: MONITORING REQUIREMENTS FOR AL-PAC WASTEWATER

Monitoring Requirements for the Alberta-Pacific Forest Industries pulp mill industrial wastewater as established by Alberta Environment, Alberta Environmental Protection and Enhancement Act Approval No. 111-01-00 through 111-01-07

Table 10.1: Al-Pac monitoring requirements for industrial wastewater

Parameters	Frequency	Sample Type
BOD ₅	3/week	composite
TSS	1/day	composite
AOX	1/week	composite
Colour	1/week	composite
Resin and Fatty Acids	1/month	grab
Toxicity Testing	see 4.2.21 and 4.2.22 ¹	grab
Flow	continuous	recorder
Temperature	continuous	recorder
BOD _U (plus COD)	1/year	composite
COD	3/week	composite
pH	continuous	recorder
Specific Conductance	continuous	recorder
TON	1/month	grab
Heavy Metals	1/year	grab
Chlorate/Chlorite	1/month	grab
Nutrients	1/month	grab
Toluene	1/month	grab
Chloroform	bimonthly	grab
Dioxins and Furans	As per Federal Regulations	composite
Ammonia – Nitrogen	1/month ¹	grab
Sulfides	1/month	grab
TOC, DOC	1/month	grab
Major Ion Analysis	2/year	grab
Total Phenols	1/year	grab
Organic Priority Pollutants	1/year	grab

¹ Section 4.2.21 and 4.2.22 detail requirements for acute lethality testing and sublethal/chronic toxicity testing, respectively.

11. APPENDIX B: SUMMARY OF RESULTS—UNEDITED DATA

Summary of raw data

Table 11.1: Results of testing at distribution box #1 (unedited)

Slug	Conductivity ($\mu\text{S/cm}$)	Temperature ($^{\circ}\text{C}$)	pH	TSS (mg/L)	BOD ₅ (mg/L)	COD (mg/L)	Colour (CU)	SOC (mg/L)	DOC (mg/L)	TOC (mg/L)	AOX Solid (mg/L)	AOX Liquid (mg/L)	AOX Total (mg/L)
1	2400	57	6.8	461	315	1229	354	88	276	363	0.2	8.0	8.1
2	2470	56	7.0	605	335	1185	188	137	260	397	0.2	5.2	5.5
3	2910	56	7.0	447	232	1331	421	107	265	371	0.8	9.8	10.6
4	2910	52	7.0	548	284	1195	370	103	248	351	0.9	9.2	10.1
5	2580	52	6.5	310	0	784	279	51	209	259	0.3	5.2	5.5
6	2520	44	6.9	355	353	837	220	108	229	336	0.4	10.2	10.6
7	2380	56	7.1	638	239	867	498	133	260	392	0.6	9.1	9.7
8	2360	51	7.1	564	407	1016	376	110	287	397	1.3	13.9	15.1
9	2390	52	7.1	479	408	1167	187	82	231	312	0.5	6.9	7.4
10	2340	49	9.6	495	289	947	232	91	219	310	0.7	3.8	4.5
11	2400	49	7.1	249	362	1159	368	110	266	376	1.8	11.5	13.3
12	2300	48	7.1	378	229	1092	235	82	194	275	1.1	8.7	9.8
13	2320	55	7.1	739	436	837	235	35	287	321	0.7	10.7	11.5
14	2900	54	7.2	1402	420	821	247	68	241	309	0.9	5.1	6.0
15	2850	55	7.0	1048	498	907	238	147	244	391	1.1	9.2	10.3
16	2270	53	6.8	419	544	1007	250	101	206	307	0.7	7.1	7.7
17	2370	59	6.8	666	525	1589	250	128	272	400	0.8	6.5	7.3
18	2730	57	6.9	1726	423	1509	250	64	215	279	0.9	6.5	7.4
19	2000	53	7.1	706	376	1126	356	102	204	306	2.2	7.0	9.2
20	2450	54	7.2	699	223	924	280	87	182	268	0.9	5.7	6.6
Average	2493	53	7.1	647	345	1076	292	96	240	336	0.8	8.0	8.8
Minimum	2000	44	6.5	249	0	784	187	35	182	259	0.2	3.8	4.5
Maximum	2910	59	9.6	1726	544	1589	498	147	287	400	2.2	13.9	15.1
Standard Dev.	248	4	0.6	365	126	226	84	29	32	48	0.5	2.5	2.7
# of samples	20	20	20	20	20	20	20	20	20	20	20	20	20

Table 11.2: Results of testing at distribution box #3 (unedited)

Slug	Conductivity ($\mu\text{S}/\text{cm}$)	Temperature ($^{\circ}\text{C}$)	pH	TSS (mg/L)	BOD ₅ (mg/L)	COD (mg/L)	Colour (CU)	SOC (mg/L)	DOC (mg/L)	TOC (mg/L)	AOX Solid (mg/L)	AOX Liquid (mg/L)	AOX Total (mg/L)
1	2410	54	6.9	158	312	814	482	65	228	293	0.0	5.0	5.0
2	2510	54	6.9	118	305	780	247	28	244	272	0.0	5.7	5.7
3	2820	54	6.5	102	236	978	423	34	264	298	0.5	4.5	5.0
4	2820	52	6.5	102	231	832	319	60	242	302	0.5	6.9	7.4
5	2340	49	6.8	288	610	929	215	83	235	318	0.6	8.8	9.4
6	2500	49	7.0	54	265	693	363	34	197	231	0.3	3.8	4.1
7	2690	52	6.8	61	270	723	808	45	220	265	0.3	4.1	4.4
8	3440	49	7.1	97	449	1139	598	79	285	364	1.2	7.3	8.5
9	2530	49	7.0	79	387	743	255	50	201	251	0.3	5.2	5.5
10	2550	47	6.9	88	196	749	274	53	199	252	0.4	5.1	5.5
11	2520	46	7.0	106	383	830	318	60	221	282	0.8	5.8	6.5
12	2250	46	7.0	52	264	832	282	34	174	208	0.4	3.7	4.1
13	2970	51	7.3	58	431	822	331	33	212	244	0.5	3.8	4.3
14	3110	50	6.9	43	370	704	267	27	199	226	0.3	3.5	3.9
15	2870	51	6.9	96	269	679	291	26	192	218	0.4	4.8	5.1
16	2320	53	7.1	83	325	608	295	25	171	196	0.3	4.1	4.4
17	2470	56	6.8	109	361	840	300	24	212	236	0.3	3.4	3.7
18	3070	55	7.0	187	309	739	300	21	202	222	0.4	4.0	4.4
19	2200	50	6.9	128	235	799	242	27	174	201	0.3	2.8	3.1
20	2700	53	7.0	124	384	580	320	22	163	185	0.4	3.9	4.4
Average	2655	51	6.9	107	330	791	347	41	212	253	0.4	4.8	5.2
Minimum	2200	46	6.5	43	196	580	215	21	163	185	0.0	2.8	3.1
Maximum	3440	56	7.3	288	610	1139	808	83	285	364	1.2	8.8	9.4
Standard Dev.	322	3	0.2	56	97	126	141	19	32	46	0.2	1.5	1.6
# of samples	20	20	20	20	20	20	20	20	20	20	20	20	20

Table 11.3: Results of testing at the cooling tower (unedited)

Slug	Conductivity ($\mu\text{S/cm}$)	Temperature ($^{\circ}\text{C}$)	pH	TSS (mg/L)	BOD ₅ (mg/L)	COD (mg/L)	Colour (CU)	SOC (mg/L)	DOC (mg/L)	TOC (mg/L)	AOX Solid (mg/L)	AOX Liquid (mg/L)	AOX Total (mg/L)
1	2560	38	7.6	122	328	682	745	52	186	238	0.1	4.4	4.5
2	2660	37	7.4	106	168	1285	623	-3	217	214	0.1	3.2	3.3
3	2640	34	7.7	143	258	755	395	72	145	217	0.5	2.3	2.8
4	2640	35	7.7	143	332	740	181	72	165	236	0.5	3.6	4.2
5	3210	35	7.2	78	160	677	354	47	158	205	0.3	2.9	3.2
6	2540	37	7.3	108	718	769	395	48	147	195	0.5	2.6	3.0
7	2780	37	7.4	68	128	693	236	66	152	218	0.4	2.6	3.0
8	3140	34	7.6	79	280	975	440	56	214	270	1.5	5.1	6.6
9	2730	35	7.6	74	240	617	362	50	134	183	0.6	2.6	3.2
10	2760	35	7.4	101	340	575	299	58	127	185	0.7	2.8	3.5
11	2760	34	7.3	126	385	864	397	109	173	283	1.1	4.1	5.2
12	2710	36	7.5	63	131	613	371	41	138	178	0.9	3.7	4.6
13	2990	36	7.5	59	404	638	320	39	141	180	0.4	2.1	2.5
14	2930	36	7.4	51	303	550	256	39	119	157	0.4	2.1	2.5
15	2660	37	7.8	71	230	586	303	44	143	187	0.5	2.6	3.1
16	2120	35	8.0	73	193	511	310	14	112	126	0.3	2.9	3.2
17	2630	37	7.9	110	194	557	305	36	136	171	0.4	1.8	2.2
18	2950	37	7.5	127	224	583	310	39	128	167	0.4	2.1	2.4
19	2140	34	7.5	100	186	607	212	33	118	151	0.4	2.0	2.3
20	2420	36	7.7	115	246	536	256	39	133	172	0.4	2.4	2.7
Average	2699	36	7.5	96	272	691	354	48	149	197	0.5	2.9	3.4
Minimum	2120	34	7.2	51	128	511	181	-3	112	126	0.1	1.8	2.2
Maximum	3210	38	8.0	143	718	1285	745	109	217	283	1.5	5.1	6.6
Standard Dev.	277	1	0.2	28	132	182	133	23	29	39	0.3	0.9	1.1
# of samples	20	20	20	20	20	20	20	20	20	20	20	20	20

Table 11.4: Results of testing at distribution box #5 (unedited)

Slug	Conductivity ($\mu\text{S/cm}$)	Temperature ($^{\circ}\text{C}$)	pH	TSS (mg/L)	BOD ₅ (mg/L)	COD (mg/L)	Colour (CU)	SOC (mg/L)	DOC (mg/L)	TOC (mg/L)	AOX Solid (mg/L)	AOX Liquid (mg/L)	AOX Total (mg/L)
1	2650	26	7.8	2245	606	2924	223	987	95	1082	3.7	0.4	4.1
2	2600	24	7.9	9288	248	1572	106	1348	139	1487	2.5	0.0	2.5
3	2490	23	7.9	4801	358	1185	179	1221	99	1320	6.3	0.7	7.0
4	2490	23	7.9	5748	338	4084	196	1467	149	1616	9.0	0.9	9.9
5	2830	24	8.0	3980	492	3300	235	1794	118	1912	7.8	0.7	8.4
6	2470	24	7.9	4602	357	5648	228	1399	99	1498	7.0	0.6	7.6
7	2880	25	7.7	3728	238	4762	253	1511	117	1628	10.9	0.8	11.7
8	3220	20	8.0	4294	505	815	541	1177	181	1358	8.9	2.0	10.9
9	2860	22	7.9	2228	173	3665	255	1039	116	1155	6.7	1.1	7.8
10	2870	25	7.7	3892	611	3478	200	1133	107	1240	8.5	0.8	9.3
11	2740	23	7.9	4226	594	3230	256	1314	101	1416	8.7	0.8	9.5
12	2960	22	7.9	3917	484	6048	300	1306	99	1405	10.0	0.9	10.9
13	3010	22	7.8	3320	445	3393	213	1219	81	1300	8.7	0.6	9.2
14	2840	25	7.8	3384	715	4670	186	1151	78	1229	7.0	0.5	7.5
15	2860	27	8.0	3472	187	4597	221	1245	112	1357	5.9	0.7	6.6
16	2300	26	8.0	3304	141	3282	215	1208	90	1297	6.8	0.5	7.3
17	2620	28	8.0	3872	248	3237	210	1368	94	1462	8.1	0.5	8.6
18	2900	29	7.9	3481	244	3291	210	1289	94	1384	7.9	0.6	8.5
19	2360	24	7.7	3258	213	4217	255	1196	89	1285	10.3	0.6	10.9
20	2790	27	7.9	3592	190	3942	240	1244	83	1327	9.7	0.6	10.3
Average	2737	24	7.9	4032	369	3567	236	1281	107	1388	7.7	0.7	8.4
Minimum	2300	20	7.7	2228	141	815	106	987	78	1082	2.5	0.0	2.5
Maximum	3220	29	8.0	9288	715	6048	541	1794	181	1912	10.9	2.0	11.7
Standard Dev.	234	2	0.1	1470	175	1321	82	177	25	184	2.1	0.4	2.3
# of samples	20	20	20	20	20	20	20	20	20	20	20	20	20

Table 11.5: Results of testing at the parshall flume (unedited)

Slug	Conductivity ($\mu\text{S}/\text{cm}$)	Temperature ($^{\circ}\text{C}$)	pH	TSS (mg/L)	BOD ₅ (mg/L)	COD (mg/L)	Colour (CU)	SOC (mg/L)	DOC (mg/L)	TOC (mg/L)	AOX Solid (mg/L)	AOX Liquid (mg/L)	AOX Total (mg/L)
1	2610	25	8.0	11	5.3	206	195	8	64	71	0.1	1.2	1.3
2	2800	23	7.9	16	4.0	150	205	5	57	62	0.0	0.9	0.9
3	2380	22	8.0	10	2.6	152	202	5	47	53	0.1	0.8	0.9
4	2380	21	8.0	25	1.9	178	207	8	59	67	0.1	1.0	1.1
5	2850	23	8.0	16	2.2	174	212	5	53	59	0.0	0.9	0.9
6	2500	23	7.8	12	3.7	165	198	15	44	59	0.1	0.8	0.8
7	2910	23	7.9	3	1.8	189	243	10	53	63	0.1	0.9	1.0
8	3220	18	7.8	31	6.2	328	496	-22	119	97	0.6	2.5	3.1
9	2970	21	7.8	20	3.5	203	252	12	62	74	0.1	0.9	1.0
10	3050	24	7.7	19	3.3	184	211	27	43	71	0.1	0.8	0.9
11	2690	22	7.8	16	3.5	180	259	22	54	75	0.1	1.0	1.1
12	2980	21	8.0	23	3.9	224	284	11	61	72	0.3	1.1	1.4
13	3180	21	8.0	10	3.4	268	228	23	51	74	0.1	0.7	0.8
14	2850	24	8.2	22	3.2	249	196	6	60	66	0.2	0.6	0.8
15	2780	27	8.1	23	2.4	181	211	7	51	58	0.2	0.9	1.0
16	2020	25	8.1	21	1.5	191	220	34	42	75	0.1	0.6	0.6
17	2430	28	8.0	16	1.6	210	215	13	38	51	0.1	0.6	0.6
18	3010	29	8.2	38	2.9	163	205	17	37	54	0.2	0.6	0.7
19	2030	23	8.0	23	2.5	182	195	15	37	51	0.1	0.5	0.6
20	2810	26	8.1	20	1.2	114	190	10	41	50	0.1	0.6	0.6
Average	2723	24	8.0	19	3.0	195	231	12	54	65	0.1	0.9	1.0
Minimum	2020	18	7.7	3	1.2	114	190	-22	37	50	0.0	0.5	0.6
Maximum	3220	29	8.2	38	6.2	328	496	34	119	97	0.6	2.5	3.1
Standard Dev.	341	3	0.1	8	1.3	46	67	11	18	12	0.1	0.4	0.5
# of samples	20	20	20	20	20	20	20	20	20	20	20	20	20

12. APPENDIX C: SUMMARY OF RESULTS—EDITED DATA

Summary of edited data.

Table 12.1: Results of testing at distribution box #1 (edited)

Slug	Conductivity (µS/cm)	Temperature (°C)	pH	TSS (mg/L)	BOD ₅ (mg/L)	COD (mg/L)	Colour (CU)	SOC (mg/L)	DOC (mg/L)	TOC (mg/L)	AOX Solid (mg/L)	AOX Liquid (mg/L)	AOX Total (mg/L)
1	2400	57	6.8	461	315	1229	354	88	276	363	0.2	8.0	8.1
2	2470	56	7.0	605	335	1185	188	137	260	397	0.2	5.2	5.5
3	2910	56	7.0	447	232	1331	421	107	265	371	0.8	9.8	10.6
4	2910	52	7.0	548	284	1195	370	103	248	351	0.9	9.2	10.1
5	2580	52	6.5	310	**	784	279	51	209	259	0.3	5.2	5.5
6	2520	44	6.9	355	353	837	220	108	229	336	0.4	10.2	10.6
7	2380	56	7.1	638	239	867	498	133	260	392	0.6	9.1	9.7
8	2360	51	7.1	564	407	1016	376	110	287	397	1.3	13.9	15.1
9	2390	52	7.1	479	**	1167	187	82	231	312	0.5	6.9	7.4
10	2340	49	9.6	495	289	947	232	91	219	310	0.7	3.8	4.5
11	2400	49	7.1	249	362	1159	368	110	266	376	1.8	11.5	13.3
12	2300	48	7.1	378	229	1092	235	82	194	275	1.1	8.7	9.8
13	2320	55	7.1	739	436	837	235	35	287	321	0.7	10.7	11.5
14	2900	54	7.2	1402	420	821	247	68	241	309	0.9	5.1	6.0
15	2850	55	7.0	1048	498	907	238	147	244	391	1.1	9.2	10.3
16	2270	53	6.8	419	**	1007	250	101	206	307	0.7	7.1	7.7
17	2370	59	6.8	666	525	1589	250	128	272	400	0.8	6.5	7.3
18	2730	57	6.9	1726	423	1509	250	64	215	279	0.9	6.5	7.4
19	2000	53	7.1	706	376	1126	356	102	204	306	2.2	7.0	9.2
20	2450	54	7.2	699	223	924	280	87	182	268	0.9	5.7	6.6
Average	2493	53	7.1	647	350	1076	292	96	240	336	0.8	8.0	8.8
Minimum	2000	44	6.5	249	223	784	187	35	182	259	0.2	3.8	4.5
Maximum	2910	59	9.6	1726	525	1589	498	147	287	400	2.2	13.9	15.1
Standard Dev.	248	4	0.6	365	94	226	84	29	32	48	0.5	2.5	2.7
# of samples	20	20	20	20	17	20	20	20	20	20	20	20	20

Table 12.2: Results of testing at distribution box #3 (edited)

Slug	Conductivity ($\mu\text{S/cm}$)	Temperature ($^{\circ}\text{C}$)	pH	TSS (mg/L)	BOD ₅ (mg/L)	COD (mg/L)	Colour (CU)	SOC (mg/L)	DOC (mg/L)	TOC (mg/L)	AOX Solid (mg/L)	AOX Liquid (mg/L)	AOX Total (mg/L)
1	2410	54	6.9	158	312	814	482	65	228	293	0.0	5.0	5.0
2	2510	54	6.9	118	305	780	247	28	244	272	0.0	5.7	5.7
3	2820	54	6.5	102	236	978	423	34	264	298	0.5	4.5	5.0
4	2820	52	6.5	102	231	832	319	60	242	302	0.5	6.9	7.4
5	2340	49	6.8	**	**	**	**	**	**	**	**	**	**
6	2500	49	7.0	54	265	693	363	34	197	231	0.3	3.8	4.1
7	2690	52	6.8	61	270	723	808	45	220	265	0.3	4.1	4.4
8	3440	49	7.1	97	449	1139	598	79	285	364	1.2	7.3	8.5
9	2530	49	7.0	79	**	743	255	50	201	251	0.3	5.2	5.5
10	2550	47	6.9	88	196	749	274	53	199	252	0.4	5.1	5.5
11	2520	46	7.0	106	383	830	318	60	221	282	0.8	5.8	6.5
12	2250	46	7.0	52	264	832	282	34	174	208	0.4	3.7	4.1
13	2970	51	7.3	58	431	822	331	33	212	244	0.5	3.8	4.3
14	3110	50	6.9	43	370	704	267	27	199	226	0.3	3.5	3.9
15	2870	51	6.9	96	269	679	291	26	192	218	0.4	4.8	5.1
16	2320	53	7.1	83	325	608	295	25	171	196	0.3	4.1	4.4
17	2470	56	6.8	109	361	840	300	24	212	236	0.3	3.4	3.7
18	3070	55	7.0	187	309	739	300	21	202	222	0.4	4.0	4.4
19	2200	50	6.9	128	235	799	242	27	174	201	0.3	2.8	3.1
20	2700	53	7.0	124	384	580	320	22	163	185	0.4	3.9	4.4
Average	2655	51	6.9	97	311	783	353	39	210	250	0.4	4.6	5.0
Minimum	2200	46	6.5	43	196	580	242	21	163	185	0.0	2.8	3.1
Maximum	3440	56	7.3	187	449	1139	808	79	285	364	1.2	7.3	8.5
Standard Dev.	322	3	0.2	37	72	125	141	17	32	45	0.3	1.2	1.3
# of samples	20	20	20	19	18	19	19	19	19	19	19	19	19

Table 12.3: Results of testing at the cooling tower (edited)

Slug	Conductivity ($\mu\text{S/cm}$)	Temperature ($^{\circ}\text{C}$)	pH	TSS (mg/L)	BOD ₅ (mg/L)	COD (mg/L)	Colour (CU)	SOC (mg/L)	DOC (mg/L)	TOC (mg/L)	AOX Solid (mg/L)	AOX Liquid (mg/L)	AOX Total (mg/L)
1	2560	38	7.6	122	328	682	745	52	186	238	0.1	4.4	4.5
2	2660	37	7.4	106	168	**	623	-3	217	214	0.1	3.2	3.3
3	2640	34	7.7	143	258	755	395	72	145	217	0.5	2.3	2.8
4	2640	35	7.7	143	332	740	181	72	165	236	0.5	3.6	4.2
5	3210	35	7.2	78	**	677	354	47	158	205	0.3	2.9	3.2
6	2540	37	7.3	108	**	769	395	48	147	195	0.5	2.6	3.0
7	2780	37	7.4	68	**	693	236	66	152	218	0.4	2.6	3.0
8	3140	34	7.6	79	280	975	440	56	214	270	1.5	5.1	6.6
9	2730	35	7.6	74	240	617	362	50	134	183	0.6	2.6	3.2
10	2760	35	7.4	101	340	575	299	58	127	185	0.7	2.8	3.5
11	2760	34	7.3	126	**	864	397	109	173	283	1.1	4.1	5.2
12	2710	36	7.5	63	**	613	371	41	138	178	0.9	3.7	4.6
13	2990	36	7.5	59	404	638	320	39	141	180	0.4	2.1	2.5
14	2930	36	7.4	51	303	550	256	39	119	157	0.4	2.1	2.5
15	2660	37	7.8	71	230	586	303	44	143	187	0.5	2.6	3.1
16	2120	35	8.0	73	193	511	310	14	112	126	0.3	2.9	3.2
17	2630	37	7.9	110	194	557	305	36	136	171	0.4	1.8	2.2
18	2950	37	7.5	127	224	583	310	39	128	167	0.4	2.1	2.4
19	2140	34	7.5	100	186	607	212	33	118	151	0.4	2.0	2.3
20	2420	36	7.7	115	246	536	256	39	133	172	0.4	2.4	2.7
Average	2699	36	7.5	96	262	659	354	48	149	197	0.5	2.9	3.4
Minimum	2120	34	7.2	51	168	511	181	-3	112	126	0.1	1.8	2.2
Maximum	3210	38	8.0	143	404	975	745	109	217	283	1.5	5.1	6.6
Standard Dev.	277	1	0.2	28	68	119	133	23	29	39	0.3	0.9	1.1
# of samples	20	20	20	20	15	19	20	20	20	20	20	20	20

Table 12.4: Results of testing at distribution box #5 (edited)

Slug	Conductivity ($\mu\text{S}/\text{cm}$)	Temperature ($^{\circ}\text{C}$)	pH	TSS (mg/L)	BOD ₅ (mg/L)	COD (mg/L)	Colour (CU)	SOC (mg/L)	DOC (mg/L)	TOC (mg/L)	AOX Solid (mg/L)	AOX Liquid (mg/L)	AOX Total (mg/L)
1	2650	26	7.8	5272	**	**	223	**	95	**	3.7	0.4	4.1
2	2600	24	7.9	4487	**	**	106	**	139	**	2.5	0.0	2.5
3	2490	23	7.9	4801	**	**	179	**	99	**	6.3	0.7	7.0
4	2490	23	7.9	5748	**	**	196	**	149	**	9.0	0.9	9.9
5	2830	24	8.0	3980	**	**	235	**	118	**	7.8	0.7	8.4
6	2470	24	7.9	4602	**	**	228	**	99	**	7.0	0.6	7.6
7	2880	25	7.7	3728	**	**	253	**	117	**	10.9	0.8	11.7
8	3220	20	8.0	4294	**	**	541	**	181	**	8.9	2.0	10.9
9	2860	22	7.9	4043	**	**	255	**	116	**	6.7	1.1	7.8
10	2870	25	7.7	4878	**	**	200	**	107	**	8.5	0.8	9.3
11	2740	23	7.9	4226	**	**	256	**	101	**	8.7	0.8	9.5
12	2960	22	7.9	3917	**	**	300	**	99	**	10.0	0.9	10.9
13	3010	22	7.8	3320	**	**	213	**	81	**	8.7	0.6	9.2
14	2840	25	7.8	3384	**	**	186	**	78	**	7.0	0.5	7.5
15	2860	27	8.0	3472	**	**	221	**	112	**	5.9	0.7	6.6
16	2300	26	8.0	3304	**	**	215	**	90	**	6.8	0.5	7.3
17	2620	28	8.0	3872	**	**	210	**	94	**	8.1	0.5	8.6
18	2900	29	7.9	3481	**	**	210	**	94	**	7.9	0.6	8.5
19	2360	24	7.7	3258	**	**	255	**	89	**	10.3	0.6	10.9
20	2790	27	7.9	3592	**	**	240	**	83	**	9.7	0.6	10.3
Average	2737	24	7.9	4083	N/A	N/A	236	N/A	107	N/A	7.7	0.7	8.4
Minimum	2300	20	7.7	3258	N/A	N/A	106	N/A	78	N/A	2.5	0.0	2.5
Maximum	3220	29	8.0	5748	N/A	N/A	541	N/A	181	N/A	10.9	2.0	11.7
Standard Dev.	234	2	0.1	703	N/A	N/A	82	N/A	25	N/A	2.1	0.4	2.3
# of samples	20	20	20	20	0	0	20	0	20	0	20	20	20

Table 12.5: Results of testing at the parshall flume (edited)

Slug	Conductivity (µS/cm)	Temperature (°C)	pH	TSS (mg/L)	BOD ₅ (mg/L)	COD (mg/L)	Colour (CU)	SOC (mg/L)	DOC (mg/L)	TOC (mg/L)	AOX Solid (mg/L)	AOX Liquid (mg/L)	AOX Total (mg/L)
1	2610	25	8.0	11	5.3	206	195	8	64	71	0.1	1.2	1.3
2	2800	23	7.9	16	4.0	150	205	5	57	62	0.0	0.9	0.9
3	2380	22	8.0	10	2.6	152	202	5	47	53	0.1	0.8	0.9
4	2380	21	8.0	25	1.9	178	207	8	59	67	0.1	1.0	1.1
5	2850	23	8.0	16	2.2	174	212	5	53	59	0.0	0.9	0.9
6	2500	23	7.8	12	3.7	165	198	15	44	59	0.1	0.8	0.8
7	2910	23	7.9	37	1.8	189	243	10	53	63	0.1	0.9	1.0
8	3220	18	7.8	31	6.2	328	496	-22	119	97	0.6	2.5	3.1
9	2970	21	7.8	20	3.5	203	252	12	62	74	0.1	0.9	1.0
10	3050	24	7.7	19	3.3	184	211	27	43	71	0.1	0.8	0.9
11	2690	22	7.8	16	3.5	180	259	22	54	75	0.1	1.0	1.1
12	2980	21	8.0	23	3.9	224	284	11	61	72	0.3	1.1	1.4
13	3180	21	8.0	10	3.4	268	228	23	51	74	0.1	0.7	0.8
14	2850	24	8.2	22	3.2	249	196	6	60	66	0.2	0.6	0.8
15	2780	27	8.1	23	2.4	181	211	7	51	58	0.2	0.9	1.0
16	2020	25	8.1	21	1.5	191	220	34	42	75	0.1	0.6	0.6
17	2430	28	8.0	16	1.6	210	215	13	38	51	0.1	0.6	0.6
18	3010	29	8.2	38	2.9	163	205	17	37	54	0.2	0.6	0.7
19	2030	23	8.0	23	2.5	182	195	15	37	51	0.1	0.5	0.6
20	2810	26	8.1	20	1.2	114	190	10	41	50	0.1	0.6	0.6
Average	2723	24	8.0	20	3.0	195	231	12	54	65	0.1	0.9	1.0
Minimum	2020	18	7.7	10	1.2	114	190	-22	37	50	0.0	0.5	0.6
Maximum	3220	29	8.2	38	6.2	328	496	34	119	97	0.6	2.5	3.1
Standard Dev.	341	3	0.1	8	1.3	46	67	11	18	12	0.1	0.4	0.5
# of samples	20	20	20	20	20	20	20	20	20	20	20	20	20

13. APPENDIX D: SAMPLING TIMES

Summary of sampling times at all five sample locations.

Table 13.1: Sample times

Slug	DB#1		DB#3		CT		DB#5		PF
1	24-Sep-01	7:55 AM	24-Sep-01	10:46 AM	25-Sep-01	2:01 PM	26-Sep-01	12:54 PM	26-Sep-01 4:24 PM
2	1-Oct-01	10:30 AM	1-Oct-01	3:23 PM	2-Oct-01	5:05 PM	3-Oct-01	5:41 PM	3-Oct-01 9:37 PM
3	8-Oct-01	10:38 AM	8-Oct-01	2:23 PM	9-Oct-01	2:13 PM	10-Oct-01	5:34 PM	10-Oct-01 9:30 PM
4	15-Oct-01	9:33 AM	15-Oct-01	1:00 PM	16-Oct-01	1:38 PM	17-Oct-01	2:26 PM	17-Oct-01 6:19 PM
5	30-Oct-01	8:27 AM	30-Oct-01	11:59 AM	31-Oct-01	1:35 PM	1-Nov-01	12:06 PM	1-Nov-01 4:22 PM
6	5-Nov-01	7:33 AM	5-Nov-01	11:10 AM	6-Nov-01	10:55 AM	7-Nov-01	11:08 AM	7-Nov-01 3:24 PM
7	8-Jan-02	7:48 AM	8-Jan-02	12:25 PM	9-Jan-02	3:13 PM	10-Jan-02	5:43 PM	10-Jan-02 10:03 PM
8	29-Jan-02	7:50 AM	29-Jan-02	11:40 AM	30-Jan-02	2:15 PM	31-Jan-02	3:54 PM	31-Jan-02 8:14 PM
9	5-Feb-02	7:40 AM	5-Feb-02	11:40 AM	6-Feb-02	3:11 PM	7-Feb-02	6:20 PM	7-Feb-02 10:44 PM
10	12-Feb-02	8:25 AM	12-Feb-02	11:35 AM	13-Feb-02	11:35 AM	14-Feb-02	9:50 AM	14-Feb-02 1:30 PM
11	19-Feb-02	8:35 AM	19-Feb-02	11:20 AM	20-Feb-02	10:40 AM	21-Feb-02	12:10 PM	21-Feb-02 4:10 PM
12	26-Feb-02	8:20 AM	26-Feb-02	11:59 AM	27-Feb-02	10:42 AM	28-Feb-02	10:00 AM	28-Feb-02 1:40 PM
13	2-Apr-02	9:05 AM	2-Apr-02	1:45 PM	3-Apr-02	6:35 PM	4-Apr-02	4:30 PM	4-Apr-02 6:15 PM
14	9-Apr-02	8:28 AM	9-Apr-02	1:30 PM	10-Apr-02	8:10 PM	11-Apr-02	6:45 PM	11-Apr-02 8:25 PM
15	11-Jun-02	8:30 AM	11-Jun-02	12:19 PM	12-Jun-02	12:35 PM	13-Jun-02	10:34 AM	13-Jun-02 2:05 PM
16	18-Jun-02	8:30 AM	18-Jun-02	12:15 PM	19-Jun-02	12:45 PM	20-Jun-02	1:30 PM	20-Jun-02 5:00 PM
17	25-Jun-02	8:00 AM	25-Jun-02	11:30 AM	26-Jun-02	11:30 AM	27-Jun-02	5:30 PM	27-Jun-02 8:35 PM
18	23-Jul-02	8:40 AM	23-Jul-02	12:33 PM	24-Jul-02	2:04 PM	25-Jul-02	1:45 PM	25-Jul-02 5:35 PM
19	30-Jul-02	8:36 AM	30-Jul-02	12:15 PM	31-Jul-02	4:37 PM	1-Aug-02	6:37 PM	1-Aug-02 10:55 PM
20	6-Aug-02	8:35 AM	6-Aug-02	12:20 PM	7-Aug-02	4:42 PM	8-Aug-02	6:52 PM	8-Aug-02 11:00 PM

14. APPENDIX E: HYDRAULIC RETENTION TIMES

Hydraulic retention time summary for each unit process during study.

Table 14.1: Hydraulic retention time summary for each sample slug.

Slug	Equalization/Cooling				Total
	Primary Clarifiers	Pond	Bioreactors	Secondary Clarifiers	
1	2:51	27:14	22:53	3:30	56:29
2	4:53	25:42	24:36	3:56	59:07
3	3:45	23:50	27:21	3:56	58:52
4	3:27	24:38	24:48	3:53	56:46
5	3:32	25:35	22:31	4:16	55:55
6	3:37	23:45	24:12	4:16	55:51
7	4:37	26:48	26:30	4:19	62:15
8	3:50	26:35	25:39	4:19	60:24
9	4:00	27:31	27:09	4:24	63:04
10	3:10	24:00	22:15	3:40	53:05
11	2:45	23:20	25:30	4:00	55:35
12	3:39	22:43	23:18	3:40	53:20
13	4:40	28:50	21:55	1:45	57:10
14	5:02	30:40	22:35	1:40	59:57
15	3:49	24:16	21:59	3:31	53:35
16	3:45	24:30	24:45	3:30	56:30
17	3:30	24:00	30:00	3:05	60:35
18	3:53	25:31	23:41	3:50	56:55
19	3:39	28:22	26:00	4:18	62:19
20	3:45	28:22	26:10	4:08	62:25

15. APPENDIX F: RETENTION STUDY DATA

Results from retention study (fluorescence measurements).

Table 15.1: Primary clarifier retention fluorescence data

Time	Fluorescence (ppb)	Time	Fluorescence (ppb)
29-May-2000 08:02	0.080	29-May-2000 09:56	0.346
29-May-2000 08:05	0.080	29-May-2000 10:01	0.330
29-May-2000 08:09	0.073	29-May-2000 10:04	0.332
29-May-2000 08:12	0.078	29-May-2000 10:09	0.326
29-May-2000 08:15	0.075	29-May-2000 10:17	0.313
29-May-2000 08:20	0.075	29-May-2000 10:29	0.310
29-May-2000 08:23	0.081	29-May-2000 10:42	0.296
29-May-2000 08:26	0.166	29-May-2000 10:53	0.301
29-May-2000 08:30	0.409	29-May-2000 11:03	0.281
29-May-2000 08:34	0.519	29-May-2000 11:10	0.280
29-May-2000 08:38	0.500	29-May-2000 11:29	0.267
29-May-2000 08:41	0.458	29-May-2000 11:40	0.277
29-May-2000 08:44	0.469	29-May-2000 11:46	0.265
29-May-2000 08:48	0.477	29-May-2000 12:10	0.250
29-May-2000 08:53	0.482	29-May-2000 12:58	0.220
29-May-2000 08:57	0.477	29-May-2000 13:43	0.209
29-May-2000 09:01	0.479	29-May-2000 14:24	0.193
29-May-2000 09:04	0.465	29-May-2000 14:53	0.185
29-May-2000 09:08	0.418	29-May-2000 16:13	0.160
29-May-2000 09:11	0.392	29-May-2000 18:14	0.130
29-May-2000 09:15	0.358	29-May-2000 21:00	0.106
29-May-2000 09:19	0.343	30-May-2000 01:00	0.076
29-May-2000 09:23	0.346	30-May-2000 04:02	0.075
29-May-2000 09:26	0.338	30-May-2000 05:00	0.074
29-May-2000 09:30	0.361	30-May-2000 07:19	0.075
29-May-2000 09:35	0.362	30-May-2000 11:00	0.103
29-May-2000 09:40	0.359	30-May-2000 17:11	0.102
29-May-2000 09:49	0.343		

Table 15.2: Equalization/cooling pond retention fluorescence data

Time	Fluorescence (ppb)	Time	Fluorescence (ppb)
06-Mar-2000 07:24	0.045	06-Mar-2000 12:50	0.418
06-Mar-2000 07:38	0.045	06-Mar-2000 13:19	0.423
06-Mar-2000 08:05	0.048	06-Mar-2000 13:30	0.417
06-Mar-2000 08:14	0.048	06-Mar-2000 13:46	0.403
06-Mar-2000 08:20	0.050	06-Mar-2000 14:05	0.400
06-Mar-2000 08:26	0.055	06-Mar-2000 14:49	0.388
06-Mar-2000 08:37	0.073	06-Mar-2000 15:23	0.380
06-Mar-2000 08:43	0.079	06-Mar-2000 16:05	0.371
06-Mar-2000 08:49	0.088	06-Mar-2000 16:39	0.365
06-Mar-2000 08:53	0.112	06-Mar-2000 17:21	0.338
06-Mar-2000 08:59	0.122	06-Mar-2000 17:57	0.340
06-Mar-2000 09:04	0.132	06-Mar-2000 18:43	0.337
06-Mar-2000 09:11	0.167	06-Mar-2000 21:00	0.300
06-Mar-2000 09:14	0.181	06-Mar-2000 23:30	0.283
06-Mar-2000 09:20	0.190	07-Mar-2000 02:00	0.262
06-Mar-2000 09:30	0.222	07-Mar-2000 02:07	0.263
06-Mar-2000 09:41	0.254	07-Mar-2000 02:50	0.263
06-Mar-2000 09:56	0.289	07-Mar-2000 04:00	0.258
06-Mar-2000 10:05	0.305	07-Mar-2000 05:00	0.231
06-Mar-2000 10:15	0.316	07-Mar-2000 08:10	0.211
06-Mar-2000 10:34	0.369	07-Mar-2000 11:08	0.190
06-Mar-2000 10:45	0.375	07-Mar-2000 16:20	0.158
06-Mar-2000 10:51	0.378	07-Mar-2000 20:00	0.138
06-Mar-2000 10:55	0.387	08-Mar-2000 03:00	0.123
06-Mar-2000 11:07	0.417	08-Mar-2000 07:19	0.111
06-Mar-2000 11:21	0.405	08-Mar-2000 11:39	0.101
06-Mar-2000 11:29	0.410	08-Mar-2000 16:46	0.090
06-Mar-2000 11:35	0.421	09-Mar-2000 07:20	0.075
06-Mar-2000 11:42	0.410	09-Mar-2000 11:10	0.069
06-Mar-2000 11:52	0.412	09-Mar-2000 17:15	0.065
06-Mar-2000 12:03	0.422	10-Mar-2000 07:30	0.059
06-Mar-2000 12:16	0.422	10-Mar-2000 14:20	0.057
06-Mar-2000 12:32	0.408	11-Mar-2000 07:24	0.050

Table 15.3: Bioreactor retention fluorescence data
(continued on next page)

Time	Fluorescence (ppb)	Time	Fluorescence (ppb)
19-Jan-2000 07:20	34	19-Jan-2000 11:21	138
19-Jan-2000 07:30	34	19-Jan-2000 11:27	143
19-Jan-2000 07:43	34	19-Jan-2000 11:38	162
19-Jan-2000 07:53	31	19-Jan-2000 11:44	171
19-Jan-2000 08:15	33	19-Jan-2000 11:50	176
19-Jan-2000 08:27	38	19-Jan-2000 11:56	183
19-Jan-2000 08:31	32	19-Jan-2000 12:02	177
19-Jan-2000 08:34	32	19-Jan-2000 12:08	188
19-Jan-2000 08:37	36	19-Jan-2000 12:14	197
19-Jan-2000 08:40	32	19-Jan-2000 12:20	184
19-Jan-2000 08:50	33	19-Jan-2000 12:36	202
19-Jan-2000 08:53	34	19-Jan-2000 12:45	222
19-Jan-2000 08:56	32	19-Jan-2000 12:54	222
19-Jan-2000 09:00	37	19-Jan-2000 13:04	218
19-Jan-2000 09:12	39	19-Jan-2000 13:14	232
19-Jan-2000 09:15	41	19-Jan-2000 13:24	242
19-Jan-2000 09:20	38	19-Jan-2000 13:34	248
19-Jan-2000 09:24	43	19-Jan-2000 13:44	245
19-Jan-2000 09:28	44	19-Jan-2000 13:51	255
19-Jan-2000 09:31	44	19-Jan-2000 13:57	252
19-Jan-2000 09:38	49	19-Jan-2000 14:04	252
19-Jan-2000 09:41	54	19-Jan-2000 14:15	255
19-Jan-2000 09:46	60	19-Jan-2000 14:21	253
19-Jan-2000 09:51	68	19-Jan-2000 14:29	263
19-Jan-2000 09:56	68	19-Jan-2000 14:39	264
19-Jan-2000 10:03	61	19-Jan-2000 14:46	266
19-Jan-2000 10:07	63	19-Jan-2000 15:15	273
19-Jan-2000 10:18	75	19-Jan-2000 15:20	270
19-Jan-2000 10:24	80	19-Jan-2000 15:29	267
19-Jan-2000 10:29	88	19-Jan-2000 15:42	265
19-Jan-2000 10:34	90	19-Jan-2000 15:50	262
19-Jan-2000 10:51	101	19-Jan-2000 15:59	263
19-Jan-2000 10:57	110	19-Jan-2000 16:07	261
19-Jan-2000 11:04	118	19-Jan-2000 16:32	269
19-Jan-2000 11:10	129	19-Jan-2000 16:49	258

Table 15.3 continued

Time	Fluorescence (ppb)	Time	Fluorescence (ppb)
19-Jan-2000 17:08	259	20-Jan-2000 06:08	159
19-Jan-2000 17:33	249	20-Jan-2000 09:02	152
19-Jan-2000 17:45	251	20-Jan-2000 10:58	144
19-Jan-2000 18:08	241	20-Jan-2000 13:02	138
19-Jan-2000 18:35	238	20-Jan-2000 16:20	130
19-Jan-2000 19:15	238	20-Jan-2000 20:10	124
19-Jan-2000 20:08	225	21-Jan-2000 01:45	115
19-Jan-2000 21:10	213	21-Jan-2000 05:10	110
19-Jan-2000 22:10	201	21-Jan-2000 08:40	105
19-Jan-2000 23:15	195	21-Jan-2000 13:43	99
20-Jan-2000 00:10	190	21-Jan-2000 16:45	95
20-Jan-2000 01:30	182	22-Jan-2000 01:05	85
20-Jan-2000 02:31	175	22-Jan-2000 09:00	78
20-Jan-2000 03:05	175	22-Jan-2000 18:00	73
20-Jan-2000 04:06	169	23-Jan-2000 09:00	69
20-Jan-2000 05:11	165	23-Jan-2000 18:00	67

Table 15.4: Secondary clarifier retention fluorescence data

Time	Fluorescence (ppb)	Time	Fluorescence (ppb)
21-Dec-1999 08:15	0.042	21-Dec-1999 10:07	0.232
21-Dec-1999 08:25	0.042	21-Dec-1999 10:12	0.230
21-Dec-1999 08:28	0.042	21-Dec-1999 10:17	0.229
21-Dec-1999 08:31	0.042	21-Dec-1999 10:23	0.220
21-Dec-1999 08:34	0.049	21-Dec-1999 10:31	0.219
21-Dec-1999 08:38	0.104	21-Dec-1999 10:38	0.216
21-Dec-1999 08:41	0.159	21-Dec-1999 10:45	0.214
21-Dec-1999 08:46	0.256	21-Dec-1999 10:59	0.204
21-Dec-1999 08:50	0.310	21-Dec-1999 11:18	0.195
21-Dec-1999 08:54	0.361	21-Dec-1999 11:32	0.191
21-Dec-1999 08:57	0.362	21-Dec-1999 11:51	0.183
21-Dec-1999 09:00	0.343	21-Dec-1999 12:11	0.170
21-Dec-1999 09:03	0.319	21-Dec-1999 12:31	0.161
21-Dec-1999 09:09	0.292	21-Dec-1999 12:54	0.153
21-Dec-1999 09:13	0.286	21-Dec-1999 13:35	0.134
21-Dec-1999 09:17	0.265	21-Dec-1999 14:04	0.128
21-Dec-1999 09:21	0.259	21-Dec-1999 14:34	0.119
21-Dec-1999 09:25	0.243	21-Dec-1999 15:06	0.110
21-Dec-1999 09:30	0.241	21-Dec-1999 15:42	0.102
21-Dec-1999 09:33	0.245	21-Dec-1999 16:14	0.096
21-Dec-1999 09:36	0.240	21-Dec-1999 16:44	0.089
21-Dec-1999 09:40	0.241	21-Dec-1999 17:23	0.081
21-Dec-1999 09:46	0.239	21-Dec-1999 18:10	0.076
21-Dec-1999 09:49	0.235	21-Dec-1999 19:00	0.084
21-Dec-1999 09:52	0.238	21-Dec-1999 19:28	0.068
21-Dec-1999 09:56	0.238	21-Dec-1999 20:30	0.063
21-Dec-1999 10:02	0.237	21-Dec-1999 21:20	0.059

16. APPENDIX G: PICTURES OF SAMPLING LOCATIONS

Pictures of each sampling location.



Figure 16.1: Sampling at distribution box #1



Figure 16.2: Sampling at distribution box #3



Figure 16.3: Sampling at cooling tower



Figure 16.4: Sampling at distribution box #5

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Figure 16.5: Sampling at parshall flume.

17. APPENDIX H: AERIAL VIEW OF MILLSITE

A aerial view of the millsite, including the wastewater treatment facility.



Figure 17.1: Aerial picture of the Alberta-Pacific pulp mill including the wastewater treatment system.

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